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FRONTIERS IN CHEMISTRY

Volume IV

frontiers in chemistry

VOLUME IV



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MAJOR INSTRUMENTS OF SCIENCE AND THEIR APPLICATIONS TO CHEMISTRY

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1945

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PREFACE TO VOLUMES III AND IV

The Western Reserve University Frontiers in Chemistry lectures have demonstrated their worth as a mechanism for presenting to graduate students the flow of chemical research, and for keeping industrial chemists abreast of their science. In spite of the shortage of gasoline and rubber, and in spite of the forty-eight hour work week, they have drawn an ample, an attentive, and an enthusiastic audience. They are highly appreciated in the Cleveland-Akron industrial area, and are recognized as a force therein.

The lectures are characterized by the distinction of the lecturers, by organization of their over-all subject matter, and by the effort which the individual lecturers evidently have put into their contributions. It is no wonder that, already, they have been imitated—this is to be encouraged.

The publication of these lectures in book form makes them available to a much wider audience, and allows those who have heard them to assimilate the material more completely. In many cases, the lectures are published in the colloquial style in which they were presented. This, as a matter of fact, was the request made of the lecturers. Others, however, have elaborated upon their lectures and, in some cases, developed them into striking and thoroughgoing contributions to the chemical literature.

David Rittenberg of the College of Physicians and Surgeons, Columbia University, who had delivered the lectures on "Isotopes, Recent Progress and Applications in Chemistry and Medicine," because of severe illness

was unable to provide us with the manuscript for Chapter I. A. S. Keston, also of the College of Physicians and Surgeons, was kind enough to write, on very short notice, an original article on the subject of Dr. Rittenberg's lectures. We wish to express our appreciation to Dr. Keston for the time and effort he has devoted to the preparation of his contribution.

April, 1945

R. E. BURK
OLIVER GRUMMITT

PREFACE TO VOLUMES I AND II

The burdens of keeping abreast with the forward movement of science must be felt even by the brightest minds and the most energetic souls in that profession. This problem presents itself with particular force to Universities who seek to train graduate students to be well-informed research workers. It is the custom for Universities to have a rather small number of professors who may be specialists in certain fields such as physical, organic, inorganic, and analytical chemistry; but one or a few professors in each of these fields can no longer hope to master the entire field, nor therefore to present a well-proportioned impression of the subject to graduate students.

The problem of keeping abreast of science is also an important one to industrial research departments and to the individuals therein. There is a great tendency for the individual industrial research man to work in a rather narrow practical field. He may serve well in his capacity, yet actually be less valuable at the end of a few years' work, because he may

have lost touch with broader aspects of his field and become somewhat obsolete as far as attacking a new and somewhat different problem is concerned.

To meet these difficulties, Western Reserve University conceived the idea of inviting distinguished scientists in the field of chemistry and closely related fields to be professors for a day. Each of these men presents two lectures. This gives him an opportunity to present a substantial view of his work. The lecturers who follow present somewhat different, though definitely related fields, so that at the end of a series one has what is, after all, a connected course of lectures, but one in which each lecture is given by a real expert. Thus far two courses of 12 lectures each have been presented. They have met with outstanding success, and the plan may well appeal to others.

The participants in the lectures enjoyed the personal contact with the lecturers. The reader of the following pages is not in the same fortunate position. To compensate for this lack, we have added, in the biographical part of the book, pictures of the lecturers and short biographical sketches about each of them.

R. E. BURK
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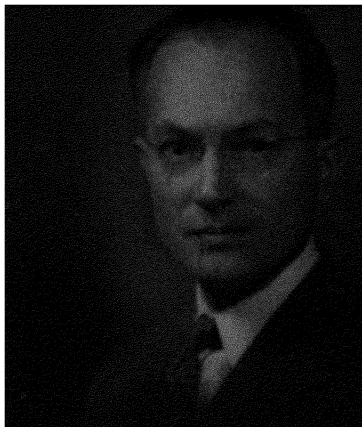


Dr. L. H. Germer, a research physicist with the Bell Telephone Laboratories, was associated with Dr. Davisson in the discovery of electron diffraction, work which furnished the first direct experimental evidence for wave mechanics, and for which he was awarded the Elliott Cresson medal in 1931. Before the war, Dr. Germer was engaged in developing electron diffraction as a research technique and in extending its usefulness. He is a leading authority in this field.

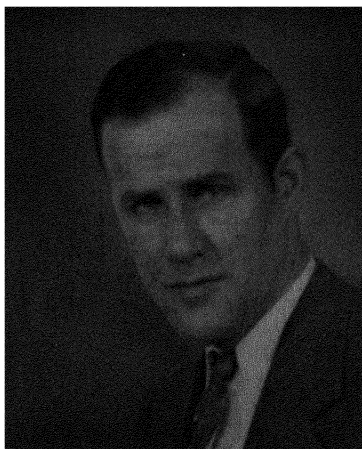


Dr. L. Marton is Associate Professor of Electron Optics and has been in charge of the Division of Electron Optics at Stanford University since 1941. Previously he worked in the same field at the University of Brussels, Belgium, and at the research laboratories of the R. C. A. Manufacturing Company in Camden, N. J. His contributions to electron optics date from the beginnings of research in this field. Dr. Marton was the first to apply the use of electron microscopes to the examination of biological and chemical objects. He is at present Chairman of the Division of Electron and Ion Optics of The American Physical Society, and Director of the Electron Microscope Society of America.

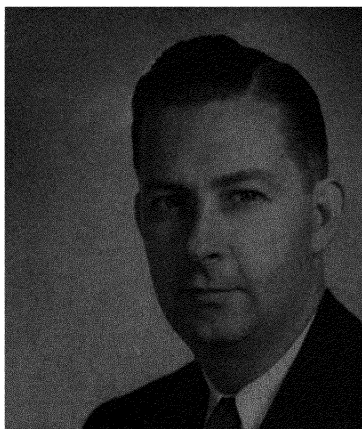
Dr. Maurice L. Huggins, now research chemist with the Eastman Kodak Company, had previously been a National Research Fellow at Harvard University, the University of California, and the California Institute of Technology, and a member of the staff of Stanford University and The Johns Hopkins University. He has been Chairman of the National Research Council Committee on X-Ray and Electron Diffraction and President of the American Society for X-Ray and Electron Diffraction. In 1941 Dr. Huggins was awarded an A. Cressey Morrison Prize by the New York Academy of Sciences. He is well known for his work on the structure of atoms, molecules and crystals, on interatomic and intermolecular forces and distances, and on the properties of large molecules.



Dr. Wallace R. Brode, Professor of Chemistry at The Ohio State University, is an authority in the field of absorption spectroscopy and spectrographic analysis. He is chairman of the National Research Council Committee on the Application of Spectroscopic Methods to Chemistry. He is the author of the well-known reference book, *Chemical Spectroscopy*, as well as an associate editor of the *Journal of the Optical Society of America*. Dr. Brode has recently completed for the W.P.B. a survey on available spectrographic standards which has been published under joint authorship by the American Society for Testing Materials. He is author of over seventy papers in American and foreign journals covering the field of absorption and emission spectroscopy.



Dr. R. Bowling Barnes is Director of the Physics Division of the Stamford Research Laboratories of the American Cyanamid Company. He had previously been a National Research Fellow at the University of Berlin and a member of The Johns Hopkins University and Princeton University. He is one of the foremost investigators of the application of optical methods to chemical problems. Although concerned with various branches of applied physics, Dr. Barnes has always devoted a major portion of his time to new developments in the field of infrared spectroscopy, and with his co-workers has reported several new applications of this tool.



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I. *Electron Diffraction and the Examination of Surfaces*

LESTER H. GERMER

Bell Telephone Laboratories, New York, N. Y.

T

I. INTRODUCTION

THE DIFFRACTION OF ELECTRONS by crystalline and pseudocrystalline materials has become a method of procedure for various chemical and physical investigations. Electron diffraction is thus an immediate "practical" application of the wave nature of matter. This is a position which it shares with the electron microscope, although the latter would probably have been invented independently of wave mechanics and its present technical development would not have led to the discovery of electron waves.

The effectiveness of the electron-diffraction method in obtaining desired information can be judged from the fact that it is being used in this country in thirty or forty laboratories, divided about evenly between educational and industrial institutions. Much of the electron-diffraction work of these laboratories has been published in about 300 scientific papers, and about 700 papers have been published dealing with similar work carried out in foreign laboratories.

Of all these investigations, many are pioneer studies connected with the discovery of the diffraction of electrons and with the observation of the phenomenon under various conditions. Others, and especially the more recent investigations, are more properly the application of the electron-diffraction technique to various problems of more or less immediate and practical importance. Researches of the latter type only will be con-

sidered here. Since, furthermore, there exist comprehensive summaries of the literature on the subject, it seems undesirable to include any extensive bibliography or any account of more than a very few of the studies which have been made. This chapter will deal first very briefly with the fundamentals of the experimental technique, then with a consideration of the fields of usefulness of electron diffraction, and finally with some selected researches upon the structure of exceedingly small particles and exceedingly thin films.

II EXPERIMENTAL METHOD

It is customary to produce electron diffraction patterns by the scattering of a beam of electrons of uniform speed. The speed, v , determines the electron wave length λ through the de Broglie formula, $\lambda = h/mv$. The wave length usually employed is of the order of 5×10^{-10} cm. corresponding to electrons which have been accelerated by a potential difference of about 50 kv. The electrons of the primary beam must receive this acceleration in a vacuum chamber. After acceleration and collimation the electron beam is scattered by the experimental specimen and the diffraction pattern of the specimen is recorded on a photographic plate placed perhaps 50 cm from it and normal to the beam. The evacuated chamber in which the electrons are produced, accelerated, collimated, scattered and recorded is commonly called an electron diffraction camera. It is attached to vacuum pumps, and is equipped with means for adjusting the specimen and the photographic plate while the camera is exhausted.

A photograph of the camera used in the *Bell Telephone Laboratories* appears as Figure 1. A description of an earlier model of this apparatus was published several years ago (1). Most experimenters have built their own cameras, many of which have been described in the literature (see, for example, the bibliography of Thomson and Cochrane, footnote below).

An up to date account of most electron diffraction investigations is in the book by Thomson and Cochrane *Theory and Practice of Electron Diffraction*. Macmillan London 1939. The many determinations of molecular structure by electron diffraction are well described in three papers by L O Brockway 'Electron Diffraction by Gas Molecules' *Rev Mod Phys* **8**, 231-266 (1936) by J Y Beach 'Electron Diffraction Investigation of the Structure of Gas Molecules' *Recent Advances in Surface Chemistry and Chemical Physics, Publications of the A A A S* No 7 88-97 (1939) and by L R Maxwell 'The Electronic Diffraction Method' *J Optical Soc Am* **30**, 374-395 (1940). From among a number of other general treatises on the subject of electron diffraction I wish to list here only F Kirchner 'Elektroneninterferenzen und Roentgeninterferenzen' *Ergeb Naturw* **11**, 64-132 (1932) and G I Finch and H Wilman 'The Study of Surface Structure by Electron Diffraction' *ibid* **16**, 353-436 (1937).

Since an electron microscope can be modified to function as a diffraction camera (2), this type of equipment may become widely used.

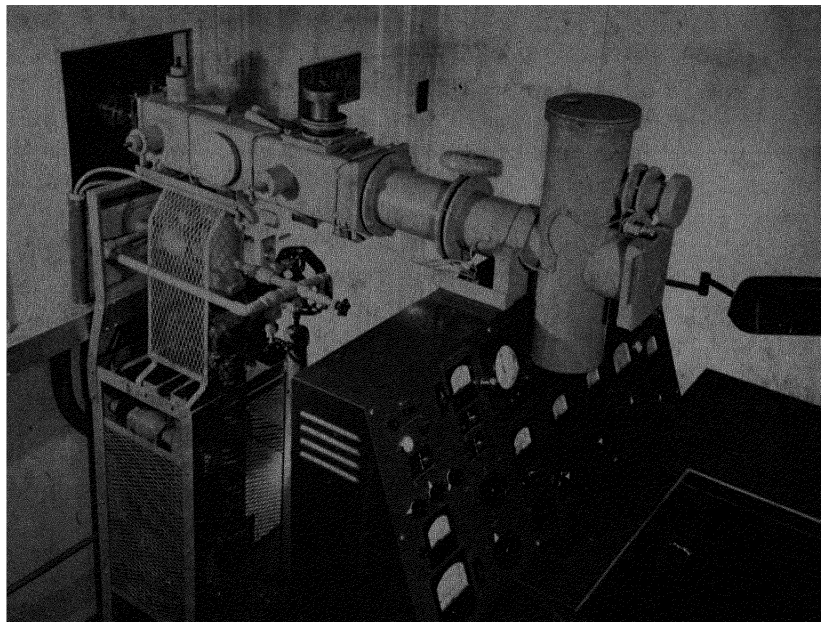


Fig. 1.—Electron-diffraction camera used in the *Bell Telephone Laboratories*.

III. FIELDS OF USEFULNESS OF ELECTRON DIFFRACTION

Electron diffraction has been applied to the determination of the arrangement of atoms both in molecules in the gaseous state and in solid bodies. Although the former is the more systematically developed field of usefulness (3), it will not be considered here. We shall be concerned only with the diffraction of electrons by solid bodies, or rather with conclusions regarding the structure of solid bodies which can be drawn from the way in which they diffract electrons.

The atomic structure of solid bodies is precisely the type of information obtained by the methods of x-ray diffraction. Yet, because x-rays are very penetrating and electrons of the speeds which are commonly used are strongly scattered and thus penetrate very slightly, the fields of usefulness of the two techniques do not greatly overlap. If one attempts to describe

the weakening of a primary beam of electrons of 50 kv. equivalent speed in a mica crystal by means of an absorption coefficient μ , one obtains $\mu \sim 2 \times 10^5 \text{ cm.}^{-1}$ (4). For heavy metals it would be considerably larger. Translated into empirically useful language, one can state that information regarding the structure of a material made up predominantly of heavy atoms (atomic number of the order of 75) can be obtained only when the experimental conditions are such that the path of the electrons in the material is considerably less than 10^{-5} cm. in length. Suitable *upper limits* for length of path vary from about 500 Å for gold to 2000 Å for magnesium.

From these estimates of penetrating power, it is clear that electron diffraction can be used to investigate only the structure of extremely thin films and extremely thin surface layers. Thus, its field of usefulness is limited, but it is limited to a region which is in many cases of great fundamental and practical interest and which cannot be so adequately studied by any other known method.

Within its restricted field, electron diffraction can be put to various uses. The most widely developed of these uses, leaving out of account investigations of the structure of gaseous molecules, is in microchemical analysis. An electron-diffraction pattern from a solid block is characteristic of the material at its surface. Comparison of the pattern from an unknown material on the surface of a block with patterns obtained from known materials can enable one to identify the unknown. For this type of analysis to be effective it is necessary that patterns from a large number of substances be observed and recorded in accessible form. A tabulation of the crystal spacings, and relative intensities of the corresponding reflections, for 1000 materials in powder form has been published by Hanawalt, Rinn and Frevel (5). A committee of the National Research Council, under the direction of Dr. Wheeler P. Davey of Pennsylvania State College, is engaged in assembling and publishing sets of spacings for a larger number of compounds. The actual structures are available (6) for many compounds for which powder patterns happen never to have been recorded; identification of one of these appearing as an unknown substance at the surface of a block can frequently be made, although not so readily as if the powder pattern data were available.

This method of chemical identification by means of an electron-diffraction pattern is similar to identification from an x-ray pattern. Either diffraction method yields more detailed information than any other analytical procedure: it determines not only what chemical elements are present but also just how they are combined, and, if the crystal structure of the material is already known, precisely how the atoms are arranged in

the crystals. In addition, either method will in general give a great deal of information in regard to the crystals themselves: information in regard to their average size; whether or not they are randomly oriented and, if not, quantitative data on the distribution in orientation; whether or not the crystals are seriously strained; even in some cases data regarding shapes of the crystals.

Since an x-ray pattern is produced by the body of a block and an electron pattern by its surface layers only, in some cases only the former yields useful information, and in other cases only the latter. In many instances, the two diffraction patterns are characteristic of different compounds or the same compounds in different proportions, and the patterns supplement each other, both being necessary for the knowledge which is desired. As an illustration of the need for both types of analysis, one can cite studies of the oxidation and reduction of iron under conditions which are industrially important. For example, the electron-diffraction pattern of Figure 2

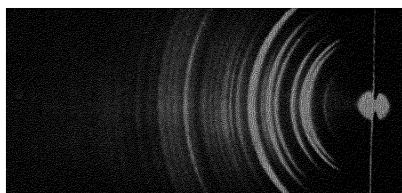


Fig. 2.—Electron-diffraction pattern of Fe_2O_3 obtained from the surface of an iron plate.

from the surface of an iron plate can be identified as due entirely to the oxide, Fe_2O_3 ; but the strongest lines of an x-ray pattern from this plate are those of Fe_3O_4 with weaker lines of iron and still weaker lines of Fe_2O_3 . From the two patterns one can conclude that the iron was covered by a layer of Fe_3O_4 about 10^{-3} cm. thick on the surface of which was a 10^{-4} cm. layer of Fe_2O_3 .

In the analysis of an unknown material from its x-ray pattern, the identification can be greatly aided by a supplementary spectroscopic analysis to determine the chemical elements which are present. In fact, in a laboratory where such analyses are frequently made, it may be the usual procedure to carry out the spectroscopic analysis first, and to follow this by the x-ray analysis. On the other hand, identification from electron patterns cannot in general be aided by spectroscopic analysis. The surface layers which produce the electron patterns are frequently too thin to per-

mit a spectroscopic analysis to be made. If they were not too thin, then probably the x-ray method would be applicable; and the latter is always more convenient if the layer to be studied is sufficiently thick. Because of technical difficulties such as those arising from an unfavorable surface contour of the specimen, and because aid cannot, in all cases at least, be obtained from spectroscopic or ordinary microchemical analysis, identification of a surface film from its electron-diffraction pattern is in general more difficult than the identification of the bulk material from its x-ray pattern. Yet the electron-diffraction method is being widely used in industrial laboratories and elsewhere for the identification of surface films because of the precise knowledge which it is capable of giving and because in a great many cases there is no other available method.

Although microchemical analysis of surface layers is at the present time the most widely developed use of electron diffraction from solid bodies, analyses of this sort are not the subject of the bulk of the papers on electron diffraction, nor is microchemical analysis as such by any means the most interesting application. Others are extremely diverse and poorly systematized, but they seem at present to offer potentialities of great future development.

One thinks at once of using electron diffraction to obtain information about catalytic processes. Although catalytically active surfaces are being studied by electron diffraction in some industrial laboratories, one cannot judge how extensive and how successful this work is because very few of the results have been published (7).

From a great number of diverse applications of electron diffraction, I have chosen to describe here three which have to do with particles of sub-colloidal dimensions, or with films only a few molecules thick. The choice was arbitrary and dictated by familiarity with the researches. These studies can perhaps be thought of as belonging to a branch of science appropriately described as surface chemistry or surface physics. Thought of in this way they are representative of the most interesting, and, although the least well developed, perhaps ultimately the most important of the uses which can be made of electron diffraction. They illustrate furthermore the extreme sensitivity of the method in its application to very small amounts of material.

IV. ELECTRON-DIFFRACTION STUDIES

1. Diffraction of Electrons by Small Crystals

By using an extremely thin organic foil as a support, very small amounts of various elements and inorganic compounds have been studied by elec-

tron diffraction by the transmission method (8). With a foil as thin as 100 Å, electron scattering from the foil makes an inappreciable addition to the scattering pattern from a deposited layer of heavy metal atoms as thick as, or thicker on the average than, two or three atomic layers. The method is therefore adaptable to the determination of the arrangement of atoms in exceedingly thin films.

In one series of experiments, diffraction patterns have been obtained from films of widely different mean thicknesses and of various materials

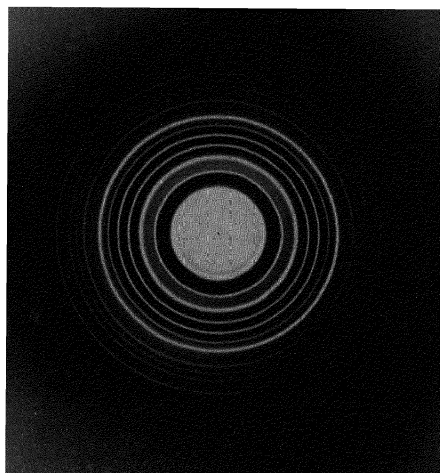


Fig. 3.—Diffraction pattern from a film of cesium iodide of 30 Å mean thickness (8).

deposited in vacuum upon a Formvar supporting foil by vaporization from a tungsten ribbon. A pattern from a cesium iodide film of 30 Å mean thickness is reproduced as Figure 3. From estimated breadths at half maximum ΔR of the rings of this pattern, one can calculate the mean crystal size C by means of the well-known Scherrer formula, which can be written in the form $C = L\lambda/\Delta R$, where $L\lambda$ is the product of the specimen-plate distance and the electron wave length. In this manner one determines that the crystals of cesium iodide in this film have average linear dimensions of about 200 Å. This value, together with the fact that the amount of deposited material was sufficient to form a layer only 30 Å thick on the average, leads to the inevitable conclusion that under the conditions of formation of the film the molecules are unstable when spread out uniformly and that they cluster at once into quite large crystals.

Somewhat similar deductions have been drawn regarding conditions of stability in films of many different substances, although in many cases the mean crystal size has been found to be much smaller than 200 Å. In particular, metal atoms in general form smaller crystals than do molecules of most inorganic compounds which have been investigated.

A rather extensive study of copper films has been carried out, the metal in these experiments being vaporized upon supporting Formvar foils within the diffraction camera itself, in order that in each test a diffraction pattern could be obtained without exposing the freshly prepared film to oxidation in the air. The films of copper studied have had various mean thicknesses, the greatest being 780 Å, and the least 3 Å, which is only slightly larger than the diameter of a copper atom. All films thicker than 20 Å produce diffraction patterns characteristic of the face-centered cubic structure in which copper crystallizes. The sharpness of the rings varies somewhat from one pattern to another, the rings of the patterns from the thicker films being narrower than those of the patterns from the thinner films. This variation of sharpness arises from differences in mean crystal size in the different films, the calculated size varying from about 70 Å in the thickest films to 50 Å in 20 Å films. It is clear in the first place that crystals are never larger than 70 Å no matter how thick the film, and in the second place that in films as thin as 20 Å the originally uniform distribution of atoms is unstable and they draw together to make 50 Å crystals.

Diffraction patterns from films thinner than 20 Å appear at first to be qualitatively different. The rings are not only broader than those from thicker films, but they appear to be altered in relative intensity so that a pattern can no longer be recognized as that of face-centered cubic crystals. The interpretation of this is quite simple. A spherical crystal of copper of 20 Å diameter contains somewhat less than 400 atoms. The resolving power of crystals of this size is sufficiently good so that a resulting powder pattern will be readily recognized as that of face-centered cubic crystals. If, however, the number of atoms in the individual crystals is much less than 400, the resolving power will be so poor that the characteristic "face-centered cubic reflections" are no longer distinguishable. In Figure 4 are given calculated scattering curves for randomly oriented spherical or near-spherical face-centered cubic crystals containing various small numbers of atoms. (In order that these curves shall be applicable to crystals of different metals, the atomic scattering factor of copper has not been included in the calculation; this would introduce a factor which is continuously decreasing with increasing angle.) The locations, Miller indices, and relative intensities of reflections from extended face-centered cubic crystals

are indicated at the bottom of the figure. By comparing these with the calculated scattering curves above, it is clear that crystals containing 379 atoms will produce a pattern from which the face-centered cubic arrangement-

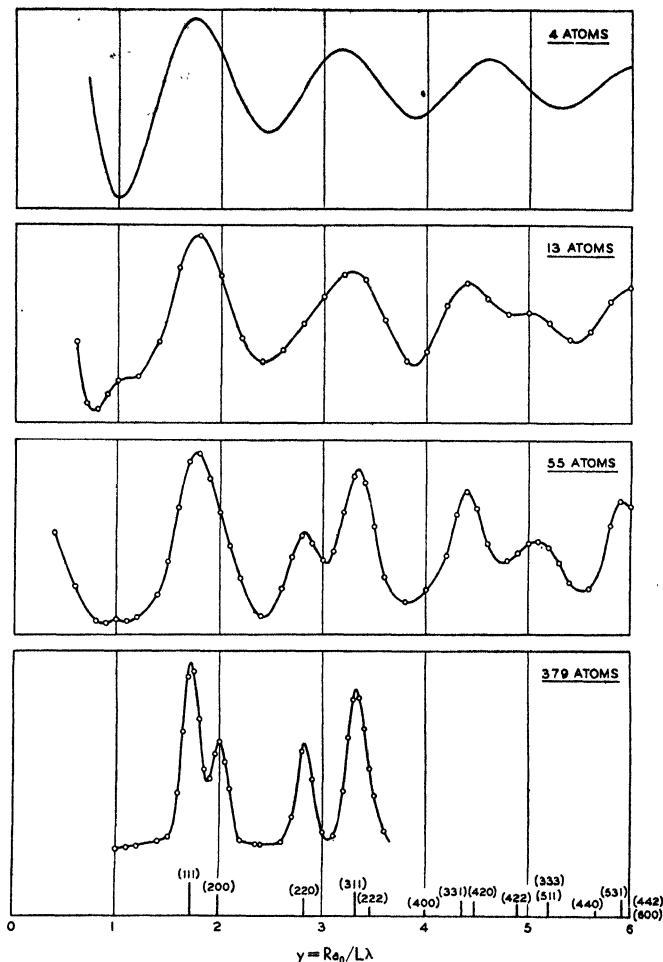


Fig. 4.—Theoretical scattering curves from randomly oriented face-centered cubic crystals made up of various numbers of atoms (8).

ment of atoms can be readily deduced, but that crystals of 55 atoms or any smaller number cannot be interpreted in this manner. It would certainly be utterly impossible to interpret an experimentally observed pattern like

the calculated pattern for 55-atom crystals, unless one had independent reasons for suspecting a face-centered cubic structure.

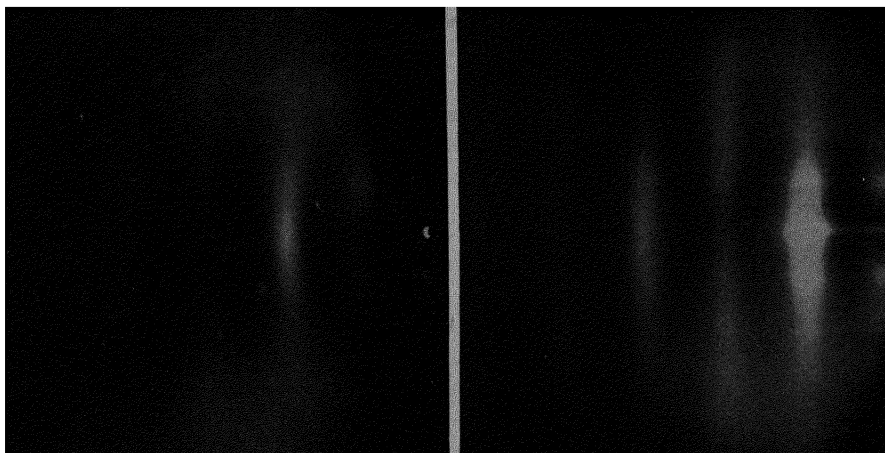
When the electron-scattering pattern from the film of copper of 3 Å mean thickness is compared with the calculated curves of Figure 4, it is discovered that the experimental pattern is intermediate in character between the curve for the 379 atom crystals and that for crystals of 55 atoms. Thus it appears clearly that the anomalous patterns obtained from extremely thin copper films are accounted for by the small number of atoms in the individual crystals and their resulting poor resolving power. It is possible to estimate from the *character* of the pattern from the 3 Å film that the individual crystals contain on the average about 200 atoms and that they are more or less equi-axed. Thus, for this thinnest film also, the originally uniformly distributed layer of atoms is unstable and crystals of appreciable dimensions are formed. For such excessively small crystals the *character* of the scattering pattern gives a quantitative measure of mean size which is a considerable extension into the extreme subcolloidal region of the range of crystal size which can be determined.

2. Arrangement of Molecules in Monolayers and Multilayers

Layers of various long chain organic molecules can be built upon the surface of a block, one layer at a time, by the well-known Langmuir-Blodgett technique in which molecules in a single layer floating upon water are transferred to the block when it moves through the water surface. Electron-diffraction patterns of such built-up layers of molecules yield information regarding the structure of the layers. The patterns are simple and readily interpreted, because in each molecule the separation between alternate carbon atoms is repeated over and over, because the carbon atoms of each molecule are coplanar, and because the molecules of any one layer align themselves with their axes parallel. The information regarding the structure of these built-up layers of long molecules is of interest in itself; but perhaps of more importance is the experience which experimenters have gained by interpreting these patterns. This has enabled them to attack successfully diffraction patterns of surface films made up of organic molecules having less simple shapes, although these latter investigations are still of a rather rudimentary character. It will suffice here to reproduce patterns obtained from a few layers of long chain molecules, to indicate how these patterns are interpreted, and to state conclusions drawn from a systematic study of built-up films containing various numbers of layers of two simple organic molecules (9).

The diffraction patterns of Figure 5 were produced respectively by a

single layer of barium stearate molecules upon the surface of a metal block, and by three layers of molecules. The separation, R , between the diffuse vertical bands of these patterns corresponds, by the Bragg formula, which can be written $Rd = L\lambda$, to a spacing, $d = 2.50 \text{ \AA}$, repeated many times in a direction normal to the surface; observation of this spacing is conclusive proof that the bands are due to hydrocarbon chains standing perpendicular to the surface. The distribution of scattering intensity is markedly different along the bands of even order from that along the bands of odd order. This difference arises from the zigzag nature of the chains and from the




a. A single layer of molecules.

b. Three layers of molecules.

Fig. 5.—Diffraction patterns from barium stearate.

fact that all the carbon atoms of each chain lie in one plane. The diffraction features lying upon the bands of Figure 5b are produced by regularities in the lateral arrangement of the molecules; and it is easy to calculate from the positions of these features that the molecules are built into a number of structures in each of which the axes of the molecules intersect the corner-points of an extended two-dimensional close-packed hexagonal net lying parallel to the surface, the side of the net being 4.85 \AA . From the absence of any diffraction features on the bands of the pattern of Figure 5a, we must conclude that in the first layer of barium stearate molecules upon the surface there is no regularity of lateral arrangement; in the first layer the molecules are packed closely together but without definite regularity.

Electron-diffraction patterns produced by stearic acid molecules built upon a metal surface show some similarities to patterns from barium stearate molecules, but there are also differences. The stearic acid molecules produce diffuse bands corresponding to the same separation of 2.50 \AA , but, whereas stearic acid molecules in the first layer stand normal to the supporting surface as do the molecules of barium stearate, in the second and subsequent layers stearic acid molecules stand with their axes inclined to the surface. The inclination to the surface is always by a definite angle which lies in the plane that was vertical when the block was dipped through the water surface. The stearic acid molecules of all layers except the first are built, furthermore, into true crystals having monoclinic symmetry. Some significant parameters of these crystals can be determined, and these parameters agree with previous knowledge of stearic acid crystals and extend such knowledge.

It is interesting to note the differences between the soap or acid molecules of the first layer and similar molecules in layers beyond the first. Molecules which touch the metal surface stand normal to it and do not possess any regularity in their lateral arrangement, but in subsequent layers molecules are built into compact crystalline arrays determined by the habit of the substances in bulk. The simplest interpretation seems to be chemical attraction between the surface and the metal atoms of the soap or the carboxyl groups of the acid, this attraction being strong enough to hold the first layer of molecules fast in certain positions which are determined by the surface atoms rather than by the natural habit of the built-up layers. 

This interpretation is supported by a series of electron-diffraction experiments upon built-up layers which have been rubbed. Rather light rubbing takes off all except the first layer of barium stearate or stearic acid molecules; but the first layer is exceedingly resistant to removal by rubbing with material which does not abrade the underlying metal itself. It is possible, by extremely light rubbing in one direction, to "upset" stearic acid molecules of all layers except the first, so that they then lie with their axes nearly, but not quite, parallel to the surface. In this condition the molecules are moderately resistant to continual light rubbing in the same direction, but they are removed by almost the lightest possible rub in the opposite direction.

3. Structure of Black Carbon

Electron-diffraction studies of what was formerly called amorphous carbon have made significant additions to our knowledge of its structure

(10). The most informative of these studies have been carried out upon carbon deposited on quartz blocks by pyrolysis of methane. The resulting carbon films are found in many cases to exhibit marked preferential orientation; and it is to this orientation that the ease of interpretation of the unusual diffraction patterns must be attributed. These patterns are more readily interpreted than those from randomly oriented carbon having the same structure for the reason that a diffraction pattern from a single crystal, which is being rotated about an important crystal direction, can yield more information than a Debye-Scherrer pattern from many small crystals.

In Figure 6 is reproduced one of the electron-diffraction patterns from pyrolytically deposited carbon having very strong orientation. The uniformly spaced heavy diffuse spots along the horizontal center line correspond to a separation of 3.66 \AA normal to the surface of the supporting block. This distance is about 9% greater than the separation between adjacent hexagonal planes in graphite; and from the result of this comparison it is natural to infer that the pattern of Figure 6 was produced by graphite-like crystallites oriented with their hexagonal planes predominantly parallel to the supporting quartz surface.

Along the vertical line at the shadow edge one can find on the original plate five pairs of diffraction features having radii which are proportional, as closely as they can be measured, to the square roots of the integers 1, 3, 4, 7 and 9. These ratios are just those of (hko) reflections from graphite crystallites, and the separation between atoms turns out to be 2.46 \AA , which is just that between atoms in the hexagonal planes of graphite. Yet the relative intensities of these reflections are not those to be expected from graphite. It is easy to discover that the intensities correspond to reflections from parallel but otherwise utterly unrelated planes of carbon atoms in each of which the atoms are arranged as in the basal plane of graphite. The intensities are quite different, on the one hand, from what they would be if the planes of atoms were built into true graphite crystals and, on the other hand, from what they would be if the atoms in the parallel but otherwise

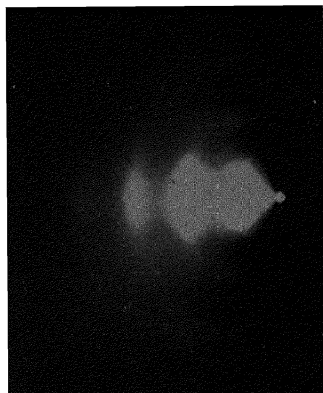


Fig. 6.—Diffraction pattern from very small oriented pseudo-crystals of black carbon (10).

unrelated planes had a close-packed arrangement (*e. g.*, the atoms in the hexagonal planes of magnesium or zinc). This deduction from the intensities of the ($h k o$) reflections is borne out by the fact that no trace whatever can be discovered of any general reflections of the type ($h k l$).

These two sets of diffraction features on the pattern of Figure 6 lead thus to a fairly clear qualitative picture of the structure of the carbon film: It is made up of sharply oriented pseudocrystals in each of which the atoms are arranged in hexagonal planes which are exactly like those of graphite. In each pseudocrystal these planes are parallel and equi-spaced by distances about 9% greater than corresponding planes in graphite. Yet there are no regularities in the lateral positions of planes belonging to the same crystal-lite, and they are therefore not true crystals at all.

These deductions, which can be made in such a very simple manner, are substantiated by transmission patterns produced by electrons which have passed *through* similar films of carbon, as well as by a more penetrating analysis of the pattern of Figure 6. This more detailed analysis, which will not be given here, leads also to quantitative values for average dimensions of the pseudocrystals and to a mathematical expression representing approximately the law of distribution of orientation of the individual pseudocrystals about the surface normal. The average dimensions discovered in this manner are very small, rather astonishingly small in fact. Parallel to the hexagonal planes it is found that the average dimension is 20 Å, or about 5 unit hexagons, and normal to these planes it is 10 or 15 Å or 3 or 4 layers of atoms.

This structure represents the most degenerate form of pseudographitic carbon. Previous x-ray investigations had revealed an extended series of carbons starting with graphite and having progressively less regular structures. By an extrapolation process in this series of x-ray studies an inferred structure had been previously assigned to this very degenerate carbon. Although this postulated structure agrees with that ascertained in the present investigation, the electron-diffraction studies give the first reliable proof of the true structure.

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NOTE

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II. *The Electron Microscope and Its Applications*

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I. THEORY OF THE APPARATUS

THE LAST TEN YEARS or so have been marked by the development of a new tool in research, the electron microscope. Greatly superior in its resolving power to the light microscope, it completes and extends the range of observation of small particles. Previous to the advent of the electron microscope, there was a gap between the molecular dimensions and the particles accessible to the light microscope which could be investigated only by rather indirect means; the electron microscope almost completely bridged this gap by making visible the particles having sizes ranging in between.

The greatly extended usefulness of the electron microscope is due to the use of a radiation with much shorter wave length than that used by the conventional type of microscopes. The useful magnification of every microscope is limited by the smallest distances shown clearly without being overmagnified in the image. The smallest distance which can be distinguished by a given optical system is related to the wave length of the radiation by the well-known law of Abbé

$$d = \frac{\lambda}{2n \sin \alpha}$$

where d is the resolved distance, λ is the wave length, n is the index of refraction of the medium and α is the angle of view of the objective lens. It

has been demonstrated that this law can be applied to the electron microscope, if λ is equal to the wave length of the wave associated with the electron, the so-called de Broglie wave length (1, 2). Its magnitude can be calculated from the formula $\lambda = h/mv$ where h is Planck's constant, m is the mass of the electron and v is its velocity. Expressed in practical units and in terms of voltage applied to the electrodes for accelerating the electron, this same wave length can be expressed as $\lambda = \sqrt{150/V}$ where V is the accelerating potential expressed in volts, and λ is measured in ångström units.

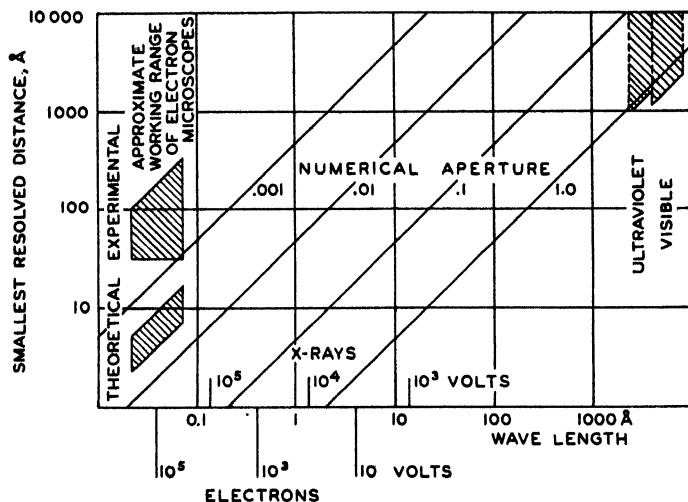


Fig. 1.—Smallest resolved distance in function of the wave length for different numerical apertures.

Light microscopes, after many years of patient research, have achieved a degree of perfection which coincides with the limit predicted by the theory. That means that the variables of Abbé's law are used to give the optimum conditions. The wave length has been lowered in the case of ultraviolet microscopes to about 2500 Å, the index of refraction has been increased to 1.68 by using convenient immersion media such as 1-bromonaphthalene, and in modern microscopes the angle of view is almost 180 degrees. Figure 1 represents the smallest resolved distance in function of the wave length for different numerical apertures ($N.A. = n \sin \alpha$). If the lines of constant numerical aperture could be extended to the very short wave length associated with the electron, distances smaller than atomic

diameters could be resolved. However, this is not the case, because electron microscopes do not operate with the high numerical apertures of light instruments.

Electron microscopy is based on the intimate analogy of the behavior between a light beam passing through lenses and an electron beam passing through electrostatic or magnetic fields of rotational symmetry. For such fields the laws governing the motion and trajectories of the electron have been calculated. The result of such calculations is that whereas, in the first approximation the laws of geometrical light optics can be completely applied to such electronic systems, great difficulties are encountered when treating the optical aberrations (3). In electron optics, not only are all the aberrations of a light optical system present, but some of them are enhanced and a few added which do not have their counterpart in light optics. At present, electron opticians are just beginning to learn a little of how to correct some of the aberrations (4, 5). The degree of correction thus achieved is small, however, as compared with the degree of correction achieved in light optics. Of particular importance in electron optics is the spherical aberration which increases with the third power of the distance from the optical axis. To achieve pictures having good resolution, the electron microscopist is obliged to use only the center part of the lenses, with the result that the numerical aperture is greatly reduced. The numerical aperture in most electron microscopes at present is about one thousand times smaller than that used in light microscopes (6, 7). However, due to the fact that a wave length is used which is one hundred thousand times smaller than the wave length of visible light, distances are resolved which are one hundred times smaller than the finest details resolved by the light microscopes. In other words, the range of useful magnification is extended by a factor of 100 (Fig. 1).

Abbé's law, combined with de Broglie's formula for the wave length of the electron, indicates a possible improvement in the resolving power for increased electron speeds (8, 9). It would appear that the higher the accelerating voltage applied to the electron microscope, the higher will become the useful magnification of the instrument. This consideration, however, does not take into account such effects, for instance, as lens aberrations. It has been found that the spherical aberration increases considerably with increasing electron speed, with the result that, for higher speeds, there is a slight decrease in useful magnification. For very high electron speeds the resolving power, however, is not the only factor determining the usefulness of an instrument. In addition, we must consider the penetration of the electron beam in the specimen and in general the

whole mechanism of image formation to judge if it is the most useful electron speed for observing a specimen.

In a transmission type of electron microscope, the image is formed not by absorption or refraction of the rays in the specimen, as in the case of light, but by the scattering of electrons produced by atoms which compose the specimen (10-12). Such scattering can take different aspects. We speak of single scattering if the specimen is thin enough so that the electron passing through it is deflected only by a single atom, and the chances for a second deflection during the passage through matter are relatively small.

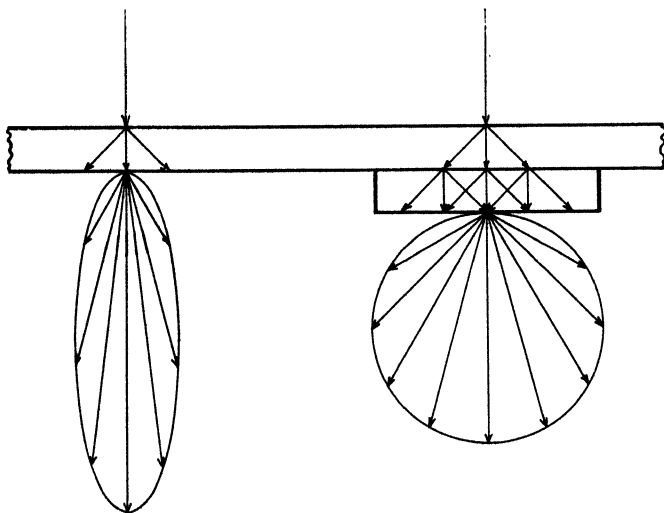


Fig. 2.—Schematic representation of electron scattering.

We speak of multiple scattering if the specimen is so thick that an electron passing through it will be deflected by a great number of atoms. Both single and multiple scattering are accessible to theoretical calculation and have been treated both by classical and quantum methods. There exists, however, an intermediate range between single and multiple scattering where the electron is subjected to a few deflections, small enough in number to make it impossible to treat them statistically but also too complicated for treatment by methods adopted in single scattering. This range is commonly known as plural scattering.

In an electron microscope the electron beam coming from the electron source and directed on the specimen by means of a condenser lens is scattered, after passing through the specimen, to different degrees corresponding to different parts of the specimen. Roughly speaking, the

scattering will be proportional to the thickness and to the density of the specimen. Only those electrons which fall within the solid angle limited by the aperture of the objective lens will contribute to the image formation. All electrons scattered beyond this solid angle are stopped by the aperture or other parts of the apparatus (Fig. 2).

Besides being a function of the thickness and the density of the specimen, electron scattering is also a function of the electron speed. A relatively thick specimen scatters the electrons so much that practically none of them will reach the objective aperture. By using electrons of higher speed, however, their mean free path in matter is increased with the result that for the same thickness and density, a greater number will reach the objective aperture. A higher electron speed thus makes possible the observation of specimens which are much too thick for lower voltages.

Besides the advantage of making the electron microscope available for the observation of thicker specimens, the use of higher electron speeds with thick specimens improves the resolving power. To understand this we must consider that every layer of matter lying between the specimen and the objective lens acts as a scattering medium. A detail of the specimen lying close to the objective lens will be imaged with the full resolving power of the instrument, but detail on the far side of the specimen will be imaged through all layers between this detail and the objective lens and be reproduced with a greatly reduced resolving power. With the use of very high electron speeds, we might, therefore, sacrifice to some extent the resolving power for the close layers if we can reduce the scattering for the back layers and thus achieve better conditions for the observation of the whole specimen.

Such observation of depth is possible by means of the electron microscope because of the enormous depth of field and depth of focus of such instruments (3). As in the case of light microscopes, the use of small numerical apertures increases the contrast, the depth of field and the depth of focus. A consequence of the greatly increased depth of field is the possibility of making stereoscopic images at high magnification. Such stereoscopic images can be produced by photographing a specimen twice, once tilted at a certain angle with the optical axis and again tilted at an equal angle in the opposite direction (13, 14). The two components of the stereoscopic image can be viewed together by means of convenient viewing devices and, if the angles of tilt are known, the depth distribution of matter in the specimen can be measured by means of known stereophotogrammetric methods. Another method of achieving the same result is tilting the incident electron beam toward the optical axis instead of tilting the specimen mechanically (12).

Tilting of the incident electron beam can also be used for the production of dark-field images. The more common way, however, of observing with dark-field illumination is to provide the condenser lens with a central spot and to use the incident beam in a mode somewhat analogous to the illumination produced by cardioid or similar condensers (15). In principle, such dark-field observations should be expected to extend the range of observation in much the same manner as dark-field observation extends the limits of usefulness of the light microscope, without improving, however, the resolving power. To date, such hopes have not been realized, and the quality of dark-field pictures taken by means of the electron microscope is considerably below the quality of bright-field images taken by the same instruments.

II. CONSTRUCTION

The practical construction of electron microscopes must take into account several factors differentiating such an instrument from light microscopes. One of the first important differences is that an electron microscope is primarily an electrical instrument operating in a vacuum. In addition to the optical requirements there are, therefore, requirements of electrical nature to be satisfied. Also its construction should, besides being sufficiently vacuum-tight, have the necessary flexibility for the operation of its various parts.

The optical requirements can be summarized as follows: Besides reduction of the lens aberrations to a minimum, the different optical elements should be aligned on an optical axis which is not necessarily a straight line as is the axis of light microscopes. Deviation from a straight line is due to the presence of stray magnetic fields which curve the electron path, of which the earth magnetic field is most important. As such stray fields might vary slowly, the optical alignment may not be maintained over long periods of time; thus it is necessary to provide an electron microscope with means for the re-aligning of its optical parts.

The electrical requirements are different in an electron microscope built up solely of electrostatic optical elements or solely of magnetic optical elements. From the approximate expression* of the inverse focal length of an electron lens

* This equation, in which V is the electric potential, H is the magnetic field strength and V_0 is the accelerating potential, is valid only for weak lenses, *i. e.*, lenses with a focal length great as compared with the extension of the field, composing the lens, along the optical axis. The lenses of electron microscopy do not satisfy this condition; the values computed by means of the correct (and very complicated) equations for such strong lenses may differ by as much as 300% from those given by the approximate expression.

$$\frac{1}{f} = \frac{1}{4\sqrt{V_0}} \int_{-\infty}^{+\infty} \frac{d^2V/dz^2}{\sqrt{V}} dz + \frac{e}{8m\sqrt{V_0}} \int_{-\infty}^{+\infty} \frac{H^2}{\sqrt{V}} dz$$

one can deduce that this focal length does not vary with the electron speed if an electrostatic lens is constructed so that the potential applied on the electrodes of the lens is the same as that applied to the electron source. In the case of a magnetic lens, however, the fluctuations of electron speed greatly affect the focal length of the lens, causing a phenomenon known in light optics as chromatic aberration. A second kind of chromatic aberration can be produced by fluctuations of the current flowing through the coils which produce the field for the magnetic lens. In a transmission type of magnetic electron microscope, a resolution of about 10 Å requires a constancy of at least one part in ten thousand of the accelerating voltage, and the constancy of the current flowing through the objective lens coil must be at least one part in fifteen thousand.

The vacuum requirements follow directly from the above-mentioned fact that electrons are scattered by matter. It is necessary to maintain in the microscope a vacuum of at least 10^{-4} to 10^{-5} mm. of mercury. Both the manipulation of the specimen and of the photographic plate must be carried out in the vacuum. Besides devices operating through vacuum-tight controls such as the stage mechanism, the photographic shutter, etc., it is often necessary to provide electron microscopes with air locks for the introduction and withdrawal of specimens and photographic plates. Such air locks are necessary because the volume of most microscopes is such that pumping to the required vacuum necessitates a period of time incompatible with practical operation of the instrument (16).

In addition to these requirements, there are some mechanical ones which must also be satisfied. The most important of the mechanical requirements is the elimination of blurring of the image through mechanical vibration. In principle, the vibrations could be eliminated by mounting the instrument in a shockproof manner; it is more reasonable, however, to follow the pattern set by modern light microscope construction and to build the instrument as a rigid unit. The most sensitive part to vibration is always the objective-object mounting, because a slight relative displacement is amplified by the whole optical system. If the instrument is built so that such relative displacements are excluded, the effect of external vibrations can be reduced beyond any observable limit.

The practical construction of electron microscopes adapts itself to the general principles contained in the foregoing paragraphs and also to the special uses for which the instrument is intended. Some instruments are

built to achieve the highest possible resolving power together with facilities for operating under unusual conditions (15, 17-24). Other instruments are built for restricted uses (25). As an example of practical instrument design, one of the latest instruments constructed at Stanford University will be described here.

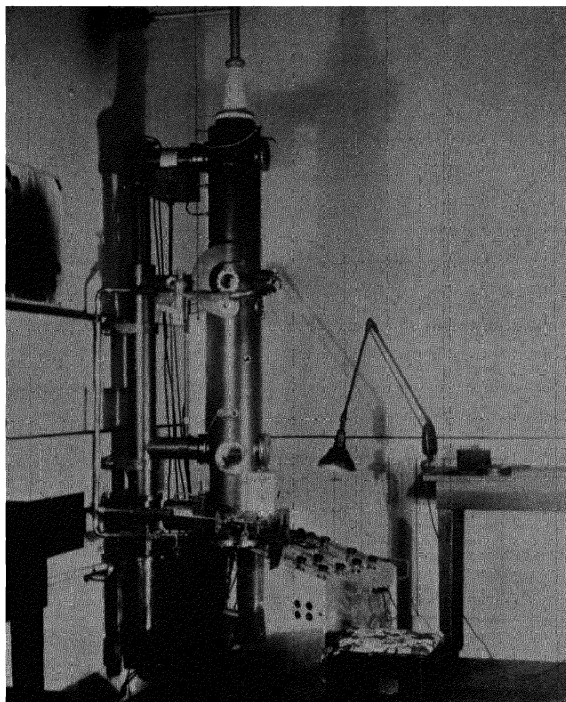


Fig. 3.—View of the electron microscope constructed at Stanford University.

An electron microscope and its electron source are built to form a single unit (Fig. 3). The reason for such design is not merely to achieve the best possible optical conditions for observation, but also because both electron source and electron microscope require a good vacuum for operation. The obvious solution is the use of a common vacuum, particularly as any matter separating the source from the optical system would introduce a scattering of the beam which might prevent or at least make difficult the operation of the instrument. The electrons are generated from a hairpin-shaped fila-

ment heated to a high temperature and accelerated by a potential of 30,000 to 100,000 volts applied on the anode. They pass through a small aperture in the anode, and the beam thus formed is concentrated on the specimen by means of a condenser lens. This condenser lens consists of a circular coil through which a current passes. The magnetic field produced by the current is concentrated on the optical axis by means of an iron enclosure of the coil and of specially shaped pole pieces.

The specimen is supported by a stage which is so constructed that, besides the conventional cross-type movement in one plane, it can be tilted

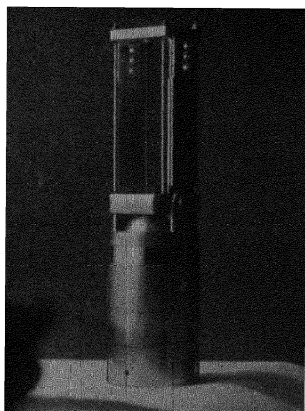


Fig. 4.—Objective lens pole-piece assembly and stage of microscope.

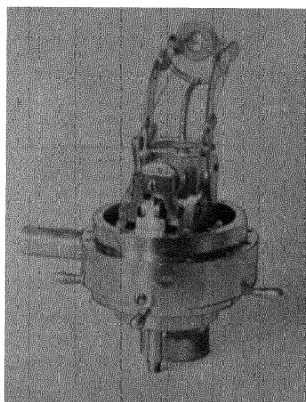


Fig. 5.—Air lock and inserting mechanism for the specimens.

at $\pm 15^\circ$. Particular care has been taken to make the stage movement very smooth. It should be kept in mind that the slightest jerkiness of the stage movement, at the high magnifications used in electron microscopes, presents a difficulty unknown in light microscopy. By making a stage completely frictionless, the jerkiness of the stage was reduced beyond any observable limit (Fig. 4).

The stage is used in the so-called object chamber of the microscope. This chamber is provided with an air lock for the introduction and withdrawal of the specimens (Fig. 5). Furthermore, the object chamber is used for the housing of flexible metallic bellows filled with a liquid to provide a hydraulic transmission of the stage movement. Capillary tubes connect the four bellows to the stage control, which is located considerably below them at a place easily accessible to the operator of the instrument (Fig. 6).

Almost every light microscope and most of the electron microscopes achieve the final magnification in two stages. In light microscopes, the two stages are called the objective lens and the eyepiece. In electron microscopes, the corresponding stages are called objective lens and projector lens, because the image instead of being observed directly by means of the eye is projected and observed on the fluorescent screen. The Stanford electron microscope achieves its final magnification in three stages, with an additional lens, called the intermediate lens, placed between the objective lens and the projector lens. All these lenses are more or less similar in design to the condenser lens described above inasmuch as they con-

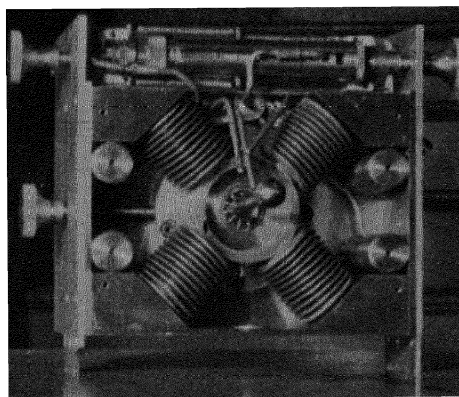


Fig. 6.—Stage control.

sist of circular coils and of iron enclosures. The differences generally manifest themselves in the shape of the pole pieces, which, for the objective lens at least, must provide a very short focal length of a few millimeters.

The magnified image can be viewed, through ports provided for this purpose, on a fluorescent screen, which serves also as a photographic shutter for the photographic plates used for the recording of the images. The photographic plates are introduced in the microscope in magazines containing 24 plates. A vacuum-tight gate is provided for sealing the magazine from the microscope when filled with air. After the magazine is filled with photographic plates, it can be pumped independently of the microscope; and when a good vacuum is reached the gate is opened again. The individual photographic plates are moved by means of a flexible tape to the center of the microscope where they can be exposed. Exposure can be partial or complete depending upon whether it is necessary to place one

single image or several partial images on the same plate. After exposure, the same type of mechanism moves the plate holder toward a second air lock, through which the plates can be individually removed from the microscope.



Fig. 7—Back view of the cabinet containing the current and voltage regulators.

The requirements of constancy of power supplies are met by elaborate circuits based on the principle of negative feedback (26, 27). Circuits have been developed which are capable of producing the stability of one part in one hundred thousand of the current passing through the lens coils of the microscope (28). It is beyond the scope of this paper to discuss such circuits in detail; Figure 7, showing the back view of the regulators of the Stanford microscope, gives a good idea of their complexity.

III. APPLICATIONS

1. Preparation of Specimens

The uses of the electron microscope cannot be discussed without mentioning the techniques needed for investigating the specimens. Since the nature of the specimens is extremely varied, ranging from biological to chemical and metallographical specimens, there is no standard way of preparing them. All techniques, however, must take into account the particular mechanism of image formation in the electron microscope and the conditions imposed by it. As mentioned before, there are limitations to the thickness of the specimen. Beyond a certain thickness which, for instance, for organic materials and electron speeds of about 60,000 to 80,000 volts is about 0.5 micron, the specimens become completely opaque and no detail can be observed. Hence one of the first requirements is that the thickness of the specimen be reduced to a minimum.

Many specimens are self-supporting, and all they need is a suitable object holder. Most such object holders in this country at present are fine wire screens (22). Many specimens, however, need further support corresponding to the slides of light microscope observation. The slides of electron microscopy must satisfy the following conditions: (1) they must be thin enough so that the scattering of the electrons by the slides is negligible as compared with the scattering by the specimen proper; (2) they should not show any structure of their own at high magnification; (3) they should be mechanically strong enough to support the weight of the specimen; and (4) they should have the necessary qualities to withstand the effects of intense electron bombardment. At present, the most common material used for such purposes is a thin film of collodion, prepared by spreading a droplet of collodion solution on a water surface and by "fishing out" the fine membranes on the wire mesh support (29-32). Besides collodion, a number of other plastics have been tried as specimen supports. Some have definite advantages over collodion: Formvar, for instance, has greater mechanical strength for the same thickness. However, they are more difficult to prepare than the collodion films and hence are less frequently used. The use of very thin layers of aluminum oxide, prepared by a slight oxidation of a smooth aluminum surface and subsequent dissolving of the metal, has also been proposed for heat-resistant specimen holders (33). In the same category belong thin layers of silica evaporated in vacuum on a smooth surface, *e. g.*, on a plastic, which can be dissolved afterwards.

Most of the specimens which can be suspended in a liquid medium are

brought on the specimen-holding membrane by placing a small droplet of the suspension on the membrane and allowing the liquid to evaporate (30, 34). A great number of chemical and biological specimens can be examined by this method. It is not necessary, however, that the dispersing agent be a liquid. When a gas or a vapor is the dispersing agent, the specimen holder is placed conveniently and for a sufficient time in the specimen-gas or vapor mixture to gather enough particles for observation. These particles may be adsorbed on the collodion film, or in some cases may simply be allowed to settle on it. In the case in which these simple processes are not satisfactory, additional means, for instance, the Cottrell process, electrophoresis, etc., can be used.

In the investigation of chemical specimens it is often found that the best way to observe is to have the particles dispersed in the solvent of the plastic film used as a specimen support. In such cases it is advantageous to have the particles cast in the material of the specimen holder. This manner of observation is closely related to the observation of the plastics and other materials which have imbedded particles which are not themselves the main object of investigation.

Another method of investigation consists of preparing replicas from the surface of specimens which otherwise are too thick for direct observation (12, 35-41). In principle, such replicas can be prepared by spreading the solution of a plastic on the surface to be studied and allowing the solvent to evaporate. Because of surface tension, the upper surface will be smooth, whereas the lower surface of the plastic will follow the contours of the specimen. After solidifying, the replica is stripped from the surface. As simple as the technique seems, the stripping generally offers great difficulties. For detailed discussion of the methods developed to avoid the difficulties, the reader is referred to the papers listed in the bibliography.

2. Colloids

The first applications of the electron microscopes were mostly of biological nature. With the improvement of electron microscopes the chemical applications follow, beginning with the investigation of some colloids and extending later to the exploration of many other fields.

The investigation of colloids includes the observation of the size and shape of colloidal particles, the extent of aggregation in function of different parameters and the investigation of adsorption reactions. From the first category we might include as a representative the investigations of von Borries and Kausche (42) on colloidal gold and the work carried out by the staff of the Columbian Carbon Company on colloidal carbon (43-45).

Both colloids belong to the category of substances which had been studied for a great number of years by all available methods. The average diameter of the particles of Micronex and acetylene black as observed in the electron microscope confirm relatively well the particle diameters obtained, for instance, by means of the low-temperature adsorption isotherm method (46).

A group of substances which have been rather extensively investigated are clays (47-58). Here, particle size distribution, shape and aggregation have been studied by a number of research workers in both this country and Germany. The particular clays which were studied included kaolinite, bentonite, montmorillonite, halloysite, endellite, attapulgite, etc. Some of the investigation was carried out in parallel with the electron microscope and with x-ray diffraction methods. It is impossible to give here an account of all the results, but it is worth while pointing out that the electron micrographs show distinctive differences between clay minerals which were not found with x-ray technique. It has also been discovered that in some cases, for instance halloysite, the proposed crystal structures do not explain the features observed in the electron microscope. In the case of halloysite, the use of different methods combined with electron microscopy indicates that this mineral is formed by dehydration of endellite.

In a similar category of substances investigated by means of the electron microscope are concrete and lime compounds. They have been extensively studied in this country and in Germany. In their work, Clark, Bernays and Tordella combined x-ray techniques with electron microscopy for the study of hydration of different lime compounds (59-63).

Metallic smokes are often used as test objects for the electron microscope (64-67). They are relatively easy to produce either by burning the metal in air or in oxygen or by producing an electric arc between the metallic electrodes and collecting the smoke particles thus produced. Magnesium oxide is commonly used for such purposes; it shows perfect cubic crystals of varying size. Sometimes the crystal size is so small that it is reduced to a chain of extremely fine particles. Often heavier particles are found supported at the end of the chain. Such chain forming is not characteristic of magnesium oxide alone, other smokes showing a chain formation of particles to a remarkable extent (Figs. 8 and 9).

By means of the electron microscope, progress has been made in the study of asphaltic substances in crude oils (68). Such asphaltic substances are precipitated during the flow of the oil from the reservoir to the stock tank. The electron microscope shows that the particles are produced by electrical charges created when the oil is streaming through the sand.

A very interesting problem which has been studied extensively by means of the electron microscope is the formation of silver particles in the photographic emulsion (69, 70). Hall and Schoen investigated the particles produced under varying conditions and found that the developed silver grain is composed of a mass of filament-shaped silver crystals, giving the whole

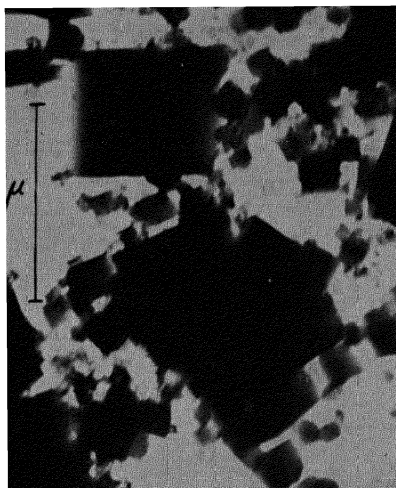


Fig. 8.—Magnesium oxide smoke from burning magnesium.



Fig. 9.—Extra-light magnesia from magnesium carbonate.

grain a more or less seaweed like appearance. From their experiments, it has been deduced that the Ostwald theory of supersaturation must be abandoned because it cannot explain the features of silver grains as observed in the electron microscope.

3. Plastics, Rubbers and Soaps

Plastics and natural and synthetic rubbers form an important group of materials which probably have been more closely investigated than many others (71). The word "probably" is used here because almost no publications are available, most of the work in this respect being part of war research. A little more has been published about investigations of the problems of the cellulose and paper industries (72-79). From the different papers dealing with this subject a few, listed in the bibliography, show that the fibers used in these industries are often much finer than would be suspected.

Curds of chemically pure soaps indicate in the electron microscope that they are composed of ribbon-shaped fibers. The width of the fibers increases in regular steps which are multiples of the double length of the soap molecule (80). Thus the electron microscope is able to produce evidence

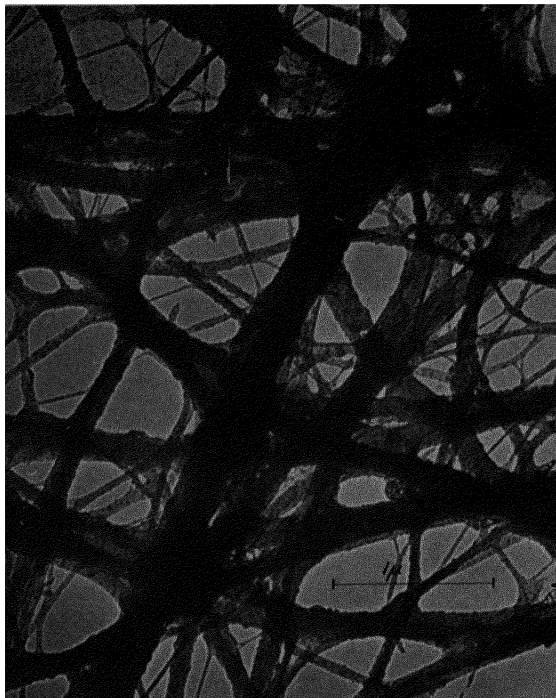


Fig. 10.—Curd fibers of sodium laurate.

for the orientation of the soap molecules in the fibers in spite of the fact that the molecules themselves are too small to be observed directly (Fig. 10).

4. Chemical Reactions

Chemical reactions can be carried out in the electron microscope and the products of the reaction observed (13, 81). They are carried out by constructing a small reaction chamber which communicates with the microscope proper through very small apertures, a procedure proposed first by Marton (82). These apertures are fine enough to let the electron beam pass but offer considerable resistance to the flowing of gas. If the

chamber is filled with a gas, a pressure of about 6 mm. Hg can be maintained between apertures when the microscope is pumped to a high vacuum. By means of such a chamber, the reactions between magnesium oxide and carbon dioxide and between zinc oxide and ammonia have been studied.

The structure of the specimens can be modified not only by means of chemical reactions, but through electron bombardment and through dehydration due to exposure to the vacuum. The influence of both factors is important enough to be studied. Whereas electron bombardment cannot be eliminated, attempts have been made to keep the specimen from being dehydrated. The first of these attempts by Marton (12) was to place the specimen between two Lenard windows, which were, however, too thick and spaced too far for good observation. A later paper (8) discusses the relation between electron speed and the useful dimensions of such enclosed cells, and comes to the conclusion that for practical dimensions considerably higher accelerating voltages are needed than those in use. Simultaneously with this paper, von Borries and Ruska described in a patent application different forms of enclosed cells.

5. Metals

Close to its chemical applications are the applications of the electron microscope to metallography. In principle, direct observation of metal surfaces at glancing angles is possible with the electron microscope (83, 84); this method, however, has not attained much popularity. The most common way of investigating metal surfaces is by means of transparent replicas (35, 37, 41, 85-87). Because of its high resolving power, the electron microscope shows a number of details which cannot be observed by other means. Slip lines, for instance, show very close spacing on many materials (*e. g.*, on aluminum about 600 Å). The interlamellar spacing on pearlite has been found on a eutectoid plain carbon steel produced by a gradient quench to be 1100 Å on the average, with a minimum of 500 Å. The precipitation causing age hardening in K-Monel metal and also in copper-beryllium alloys shows a very fine dispersion, about 300 Å in the first case and about 500 Å in the second. Cold work seems to have the effect of fragmenting the domains in copper.

Some very good replica micrographs are taken by means of a technique developed by Heidenreich and Peck (40). The replica observed in the electron microscope is, in this case (Figs. 11 and 12), a silica film produced by evaporation in vacuum on a polystyrene surface serving as an intermediate replica. Contrary to expectation from the observation of evaporated metals, which show definite graininess in structure, the silica seems to

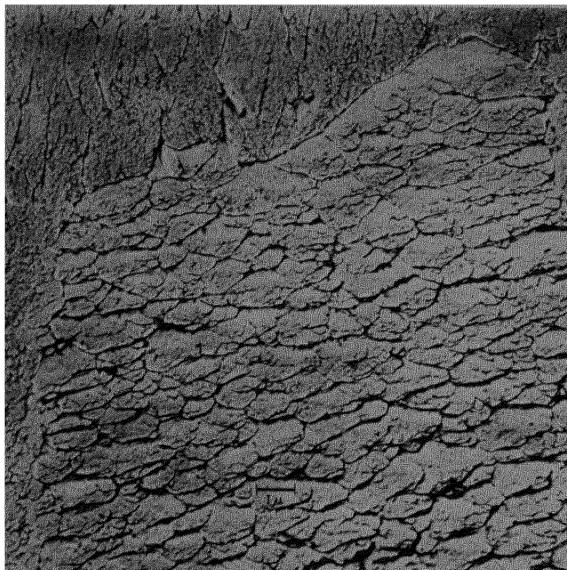


Fig. 11.—Electrolytic copper etched in ammonium hydroxide-hydrogen peroxide Polystyrene-silica replica. (Courtesy R. D. Heidenreich, *Dow Chemical Company*)

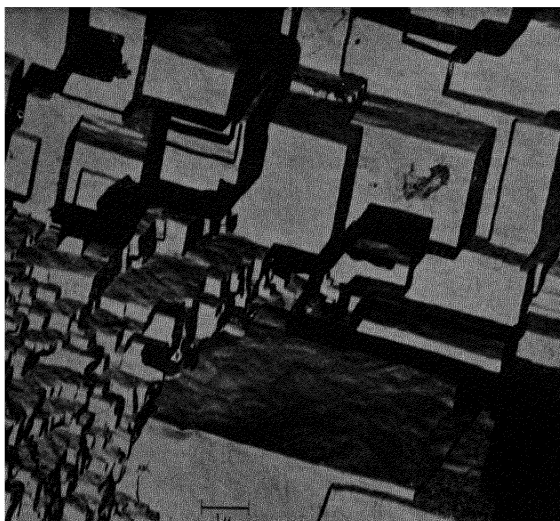


Fig. 12.—Pure aluminum etched in hydrochloric acid. Anodic oxide replica removed with mercuric chloride solution. (Courtesy R. D. Heidenreich, *Dow Chemical Company*.)

"flow" and form a continuous film with no structure of its own. The difference between the behavior of silica and of metals is very marked even though there is some kind of "flowing process" in metals. One evidence for such flowing is the change in resistivity of metallic films, made by evaporation or by cathode sputtering, occurring during the first few hours after the production of the film. Systematic investigation of such metallic films was carried out by Picard and Duffendack (88), who came to the conclusion that the observed surface formation of such films is in agreement with a theory developed by Lennard-Jones, assuming migration of the atoms over a surface. Incidentally, when dust particles are present on the supporting film and the evaporation of metal is at an angle different from normal, shadows are cast. If the angle of evaporation is known, the length of the cast shadow can be used for the determination of the height of the particle. This method has been deliberately applied recently by Müller for particle thickness determination and has given results in good agreement with determinations by means of stereophotogrammetry (89).

6. Biological Applications

The biological applications of the electron microscope, at present at least, are mostly in bacteriology and virus research. Since the first demonstration of biological application by Marton (90, 91), very little histological work has been carried out, mainly because of the thickness limitation of the specimens. The microtomes which are commonly used cannot cut sections thinner than about 2 microns, whereas the maximum thickness of the specimen for electron speeds below 100,000 volts is about 0.5 micron. An attempt to produce finer sections was made by von Ardenne in making them wedge-shaped and observing the thinnest part of the wedge (92). Recently, O'Brien and McKinley proposed using a knife rotating at extremely high speeds, and state that, by this method, sections of only 0.1 micron can be cut (93). Such a new technique may open quite a large field of research for areas hitherto unexplored by the electron microscope.

The bacteriological applications, starting with the first pictures of this nature taken by Marton (30, 94), have been very extensively developed during the last three years. The first phase of research was more or less devoted to the morphology of bacteria (95-102). A considerable number of papers has been published describing the general appearance of bacteria and their flagella. It is interesting to point out that the flagella, which in light microscopy cannot be observed without the use of special staining techniques which increase their diameter considerably, are observed in the electron microscope without stain (Fig. 13).

The second phase of bacterial research by means of the electron microscope studies the changes brought about in the appearance of the bacterial cell by mechanical or chemical agents. For mechanical actions, ultrasonic vibrations have been used, and their application seems to give strong argument in favor of the view that the bacterial cell is surrounded by a rigid membrane (103-106).

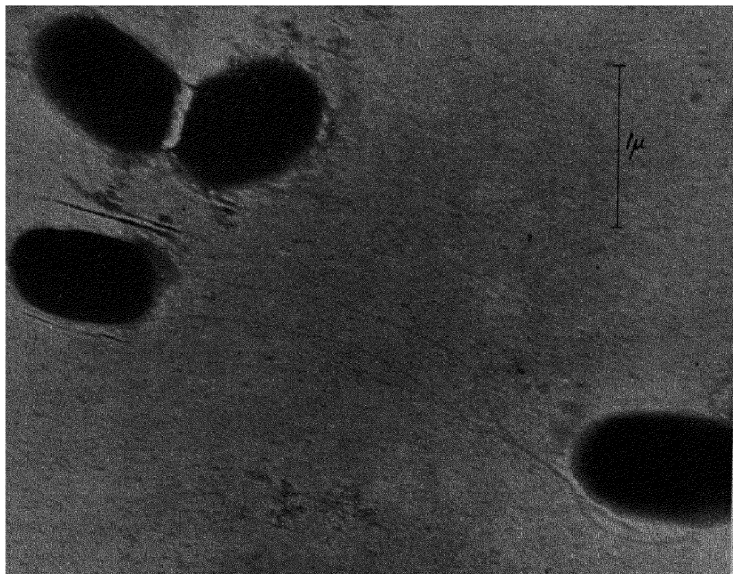


Fig. 13.—*Escherichia coli* showing flagella.

The number of chemical agents influencing the bacterial cell which have been studied up to now is relatively limited. Further work is needed before reaching definite conclusions (107, 108). To some extent, the action of bacteriophages belongs in the same category; they have been studied extensively in this country and in Germany. It has been shown that the action of the phage causes destruction of the cell wall, after which cytolysis occurs (109-113). The phage particles themselves have been revealed to possess a complex structure consisting of a "head" and a "tail," the head evidencing some internal structure.

The observation of virus particles is one of the striking applications of the electron microscope because of the extremely small size of some of the particles. Research has been carried out on the size and shape of a con-

siderable number of virus particles, and the results more or less confirm previous findings by means of different indirect methods (114-118). For instance, tobacco mosaic virus, which previous to electron microscopical observation was described as a rod-shaped particle of about 4300 Å length and about 123 Å in diameter, was found to have a length of about 3000 Å and a diameter of about 150 Å (119).

Adsorption reactions have been carried out on viruses (120, 121). It is worth remarking that, until now, such observations did not indicate whether the covering of the virus particles was complete or not. Whether this has anything to do with the unchanged infectivity of the virus proteins after the gold-sol reaction remains to be solved.

Beyond the observation of virus particles, attempts have been made to observe other protein or albumin molecules. The difficulty, due to the limited resolving power in observing small organic particles, is further increased by lack of contrast. This latter is indeed a more serious limitation than the first in dealing with such objects. It can be demonstrated theoretically that many objects, which are well within the reach of the resolving power of the instruments, can hardly be observed because the number of electrons scattered by them is too small. This explains why instruments having a resolving power of 20-25 Å do not show smaller proteins than edestin (80-110 Å particle diameter) (122-124). In principle, we possess means of doing better than that, but the difficulties are considerable. One way would be dark-field observation; it was mentioned before that to date we are unable to use it to its best advantage. A second possibility is operating with greatly reduced speed of the electrons. A third is increasing the contrast by introducing heavy atoms into the molecule, as shown in the case of benzoyl-glycogen by Husemann and Ruska (125). As this last method, however, modifies the molecule, it might be doubtful whether it should be listed as equivalent to the first two procedures.

This review of chemical and biological applications of the electron microscope necessarily cannot include all of them. Its aim has been to point out a few of the more representative applications which represent the wide variety of applications of this recent tool of scientific research.

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III. *X-Ray Diffraction and Its Applications*

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A

I. INTRODUCTION

ALTHOUGH THEY ARE INVISIBLE TO THE EYE, x-rays are of the same nature as ordinary light. Their invisibility may be attributed to their very short wave length. The wave length of x-rays is of the order of one one-hundred-millionth of a centimeter; that of visible light is in the neighborhood of one twenty-thousandth of a centimeter. X-rays are intermediate between ultraviolet rays, which have longer wave lengths, and gamma rays from radioactive substances, which have shorter wave lengths.

X-rays are best known for their ability to pass through many materials which are opaque to ordinary light. The degree of transparency of an object to x-rays varies with the thickness of the object, the kinds of atoms of which it is composed and the closeness of packing of these atoms. X-radiographs, or "shadow pictures," showing variations of one or more of these three factors, are proving of great value in medical and industrial work.

X-rays are also well known for their ability to kill or injure certain types of biological structures (cancer cells, for example)—an ability which, of itself, would make them a medical tool of paramount importance.

Our interest here, however, is not with x-radiography or x-ray therapy, but rather with the equally important field of *x-ray diffraction*. In x-ray diffraction research, one measures the directional distribution of scattered or diffracted x-rays produced when a beam of x-rays passes through a small sample, *e. g.*, a crystal or crystalline powder, of a substance, and from this directional distribution deduces certain facts about the degree and type of regularity of arrangement of the atoms in the sample.

X-ray diffraction is closely related to electron diffraction, considered in Chapter I of this volume. The principles underlying the two are essentially the same, each, however, having its special field of application. The more important differences between these two types of phenomena are the following:

(a) The wave length of x-rays used in most x-ray diffraction research is characteristic of the element in the target of the x-ray tube (see page 43); the wave length of the electrons in an electron beam depends entirely on their velocity, and changes as that velocity changes—on penetration into the sample, for example.

(b) The diffraction of electrons is altered by the Coulomb attractions and repulsions between the negatively charged electrons in the electron

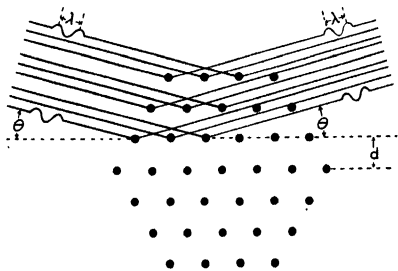


Fig. 1.—“Reflection” of x-rays (of wave length λ) by a set of atomic planes (of spacing d) in a crystal.

beam and the charged units—positive nuclei and negative electrons—of which the atoms in the sample are composed. The importance of this effect obviously depends very much on the velocity of the electrons. There is no similar Coulomb effect in x-ray diffraction.

(c) The penetrating power of electrons into a sample is much less than that of x-rays, for the wave lengths customarily employed.

(d) The time of exposure required to obtain useful data is usually much less for electron diffraction than for x-ray diffraction.

Because of these differences, electron diffraction methods are most useful in studying the structures of solid surfaces and of gas molecules, while x-ray diffraction methods are, as a rule, much better for the study of the internal structures of crystals and semicrystalline solids. Figure 1 illustrates the principle of the diffraction of x-rays by a regular arrangement of atoms, as in a crystal. Let us assume a beam of x-rays, of wave length λ , moving in a direction which makes an angle θ with a set of parallel planes

of atoms in the crystal. Let the spacing between adjacent atomic planes be d . Each atom absorbs a small amount of the energy of the x-radiation, re-emitting it in all directions. In certain directions, the radiation "scattered," *i. e.*, absorbed and re-emitted, by all the atoms in all the planes will be in phase; in all other directions, there will be destructive interference and hence no observable effect.

The geometrical requirements for cooperation of the radiation scattered by all the atoms in the atomic planes are the following:

(a) The incident beam, the diffracted (or "reflected") beam and the normal to the set of atomic planes being considered must be coplanar.

(b) The incident beam and the diffracted beam must make equal angles with the set of atomic planes.

(c) The relationship,

$$\sin \theta = n\lambda/2d, \quad (1)$$

where n is an integer, must be satisfied.

Since, in any crystalline assemblage of atoms, there are many sets of parallel planes of atoms, each set having a certain orientation and a certain value of the interplanar distance, a given crystal will give rise to "reflections" in many different directions, provided either (a) the incident beam contains a sufficient range of wave lengths, or (b) the relative orientation of incident beam and crystal is varied over a sufficient range.

II. EXPERIMENTAL METHODS

The usual source of x-rays is an *x-ray tube*, represented in simplified form in Figure 2. Such a tube is a highly evacuated vessel, in which negatively

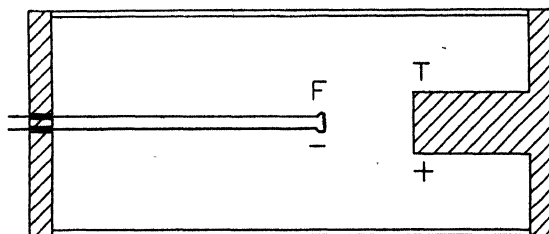


Fig. 2.—Schematic representation of an x-ray tube.

charged electrons are emitted from a hot wire filament, F . A large difference in potential, say, 40 kilovolts, between this filament and a metallic target, T , causes these electrons to move toward the latter. Their sudden deceleration on striking the target produces x-rays—"general" radiation

(corresponding to white light), having all wave lengths within a considerable range. The bombarding electrons knock other electrons from

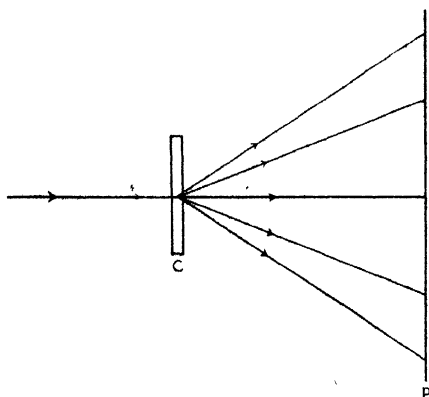


Fig. 3.—Schematic representation of the production of a Laue photograph: *C*, crystal; *P*, photographic film.

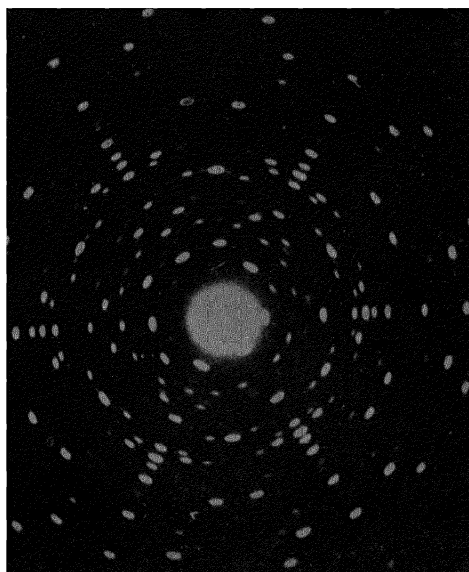


Fig. 4.—Laue photograph of a crystal of " β -alumina," $\text{Na}_2\text{O} \cdot 11 \text{Al}_2\text{O}_3$, with the x-ray beam approximately normal to the sixfold axis of symmetry.

their normal sites (orbits) in the atoms of the metal; the refilling of these sites by these or other electrons produces "characteristic" x-rays — having wave lengths characteristic of the element of which the target is composed. The characteristic x-rays emitted from a given element are chiefly of a single wave length (monochromatic), although smaller amounts of one or more other wave lengths may also be present and must be allowed for.

If the x-ray tube wall (or a "window" in it) is sufficiently transparent to the x-rays emitted from the target, they pass out of the tube, where they may be utilized for diffraction studies or other purposes.

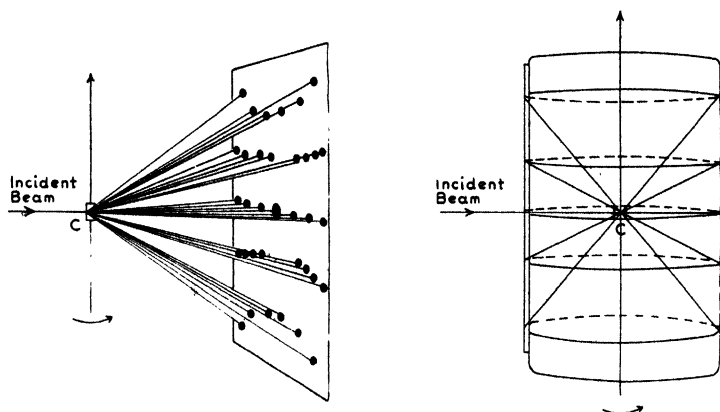


Fig. 5.—Illustrating two setups for the production of rotating crystal photographs (6b). For the powder method, the same setups may be used, crystal *c* being replaced by a cylinder of powder (which need not be rotated).

Although other methods for detecting x-rays and for measuring their intensity are occasionally used, by far the most common procedure is to employ photographic films for the purpose. X-rays affect a photographic emulsion in the same way as does ordinary light.

The most important general methods for obtaining useful x-ray diffraction data by the interaction of x-rays with one or more crystals will now be described. In each of these methods, a *beam* of x-rays is used, obtained by aligning, in front of the x-ray source, a series of two or more pinholes or slits in screens of a material, such as lead, which is relatively impervious to x-rays.

In the *Laue method*, depicted in Figure 3, a single crystal is placed in a fixed position in the x-ray beam. The x-rays should be, primarily at least, general radiation, covering a range of wave lengths. Each set of atomic

planes in the crystal reflects the wave length or wave lengths satisfying equation (1). This method is most useful in determining the symmetry of a crystalline arrangement (Fig. 4) and in studying the orientation of a crystal or crystals.

The other methods in common use employ characteristic x-radiation rather than the general radiation. The latter, which is always present in the emitted x-rays, may either be neglected or it may (for the most part) be filtered out. In the *rotating crystal method* (Figs. 5 and 6), reflections from various sets of atomic planes are obtained by rotating the crystal. The rotation varies the incidence angle, θ , for each set of planes; reflection occurs when θ has a value satisfying equation (1).

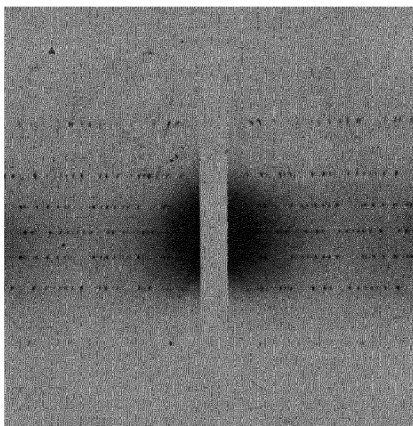


Fig. 6.—Rotating crystal photograph of silver oxalate, $\text{Ag}_2\text{C}_2\text{O}_4$. (Courtesy of R. L. Griffith.)

In the *powder method*, illustrated in Figures 5, 7 and 14 (page 54), the many small crystals are oriented in many different ways with respect to the incident beam. Some are suitably oriented for reflection by a set of planes of one type, others for reflection by planes of another type, etc. With a sufficient number of randomly oriented crystals, equation (1) is satisfied by some crystals for any given set of atomic planes, provided d is not too small.

The powder method is often the only method which can be employed, since the production of satisfactory single crystals of a given substance is frequently difficult or impossible. It is especially useful for identification

purposes (see Section IV, pages 53–54) and for the study of metals, which can be considered as aggregates of minute crystals more or less randomly oriented (Fig. 14, page 54).

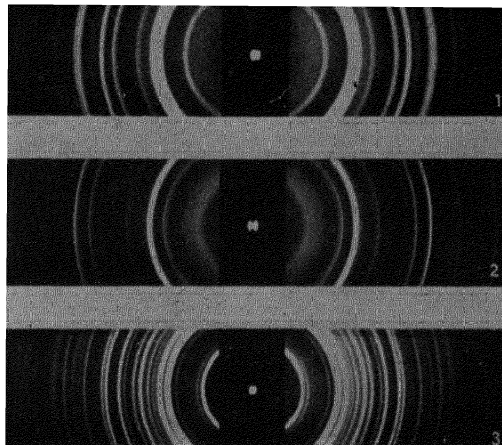


Fig. 7.—Powder photographs of (1) ferric oxide (Fe_2O_3), (2) magnetite (Fe_3O_4) and (3) silver oxalate ($\text{Ag}_2\text{C}_2\text{O}_4$). (Courtesy of R. L. Griffith.)

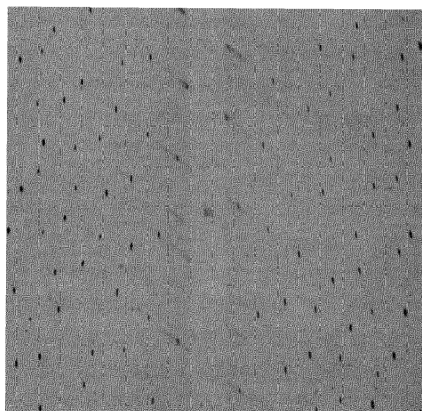


Fig. 8.—Weissenberg photograph of silver oxalate. (Courtesy of R. L. Griffith.)

The rotating crystal method and a modification of it, known as the *Weissenberg method*, are especially useful in the analysis of crystal structures

(see the next section). In the Weissenberg method, the photographic film is moved during the exposure parallel to the axis of rotation of the crystal. All reflections are blocked out except those which, in the simple rotating crystal method, would occur in a single layer line. The motion of the film spreads these reflections out in such a way as to facilitate greatly their identification: that is, the determination, for each reflection, of the orientation in the crystal of the reflecting set of planes (see Fig. 8).

III. METHODS OF STRUCTURE DETERMINATION

The first step in the analysis of a crystal structure from x-ray diffraction data is usually the determination of the shape and dimensions of the *unit cell*, which is the smallest parallelepiped, conforming to the symmetry of the crystal, which will give, by repeated translations in the directions of the crystal axes, the complete structure.

The *unit distances*, or lengths of the edges of the unit cell, are the same as the *identity distances* (the distance between consecutive points in the structure which are surrounded in identically the same manner) in the directions of the crystal axes. The identity distance along any axis can be simply computed from the distance between *layer lines* in a rotation photograph obtained with the crystal rotating about that axis (see Fig. 6). The dimensions of the unit cell may also be determined by other more complicated, but perfectly rigorous, procedures. Any tentatively assumed unit cell size and shape can be tested by computing the positions of the diffractions to be expected on that assumption. If the unit assumed is the true unit, it accounts for the positions of all observed diffraction spots and is the smallest unit which does.

The next step in a structure analysis is the computation, from the dimensions of the unit cell, the density and the chemical formula of the substance, of the number of molecules or of atoms of each kind per unit cell. These numbers must be integral.

Crystal structures may be classified according to the number and distribution of *symmetry elements*—axes, planes and centers of symmetry—which they possess. Some information about the internal symmetry may be obtained from data on the optical properties of the crystals, their external form (crystal “habit”), etc. Further information may be gained from the symmetry of the diffraction photographs, especially Laue photographs, and from the presence or absence of reflections from certain classes of planes.

Extensive tables (1) list the possible types of atomic distribution con-

forming to the various classes of symmetry ("space groups"). Using these tables, the experimental information concerning the symmetry, combined with a knowledge of the number of atoms of each kind in the unit cell, sometimes suffices to determine uniquely the atomic arrangement in a simple crystal. More often, it is necessary to make use of other information or assumptions, such as the assumption that the distance between two adjacent atoms or ions is approximately equal to the sum of their atomic or ionic radii, as computed from other structures, or the assumption that the atoms in a crystal of an organic compound are in molecular units, at least approximately conforming to the requirements of the molecular structural formula.

For complex structures, it is necessary to use the relative intensities of the diffractions and usually to employ trial-and-error and successive-approximation methods. If the structure is very complicated, these involve long, tedious calculations, and even then it has not always been possible to deduce the complete atomic arrangement.

During the past few years, powerful new procedures for analyzing complex crystal structures have been developed and the development is continuing, although slowed down by the war. By means of these procedures, one can already deduce structures of much greater complexity than those which could be studied satisfactorily by the older methods, and there is good reason to expect much more rapid progress in the future.

In the new procedures, intensity data from a large number of x-ray diffractions from the crystal being studied are combined mathematically in such a way as to give the relative values of *electron density* at different points in the unit cell or, more simply, relative values at different points in one face of the unit cell of the *projection* of the electron density in the unit. From the projected electron density values, one can draw contour maps, showing peaks where the projections of the atoms in the unit would come. Figures 36 and 37 (page 66) show such projections. Projections on two and sometimes three faces are often necessary to fix accurately the relative positions of all the atoms in the unit.

To shorten the long computations required for the direct computation of projected electron densities and to make the summations more nearly automatic, several new procedures are being developed. One of these (2) involves the use of many thousands of specially punched cards, with appropriate International Business Machines. A second procedure (3) involves the use of much electrical equipment, of types used by commercial telephone companies, in a complicated electrical hookup. In another method (4, 5), the projected image of the electron density pattern is observed through a

microscope, this image being produced by mutual interaction of light-rays passing through holes, of size and position determined by the x-ray data, in a metal plate or in an otherwise opaque photographic film. In a fourth method (6; 7), successive exposures—one for each of the observed x-ray diffractions being utilized in the summation—are made through previously prepared masks (Fig. 9), onto a single photographic film or paper. This gives directly the electron density projection desired. Development of this film or paper yields a picture in which the photographic density,

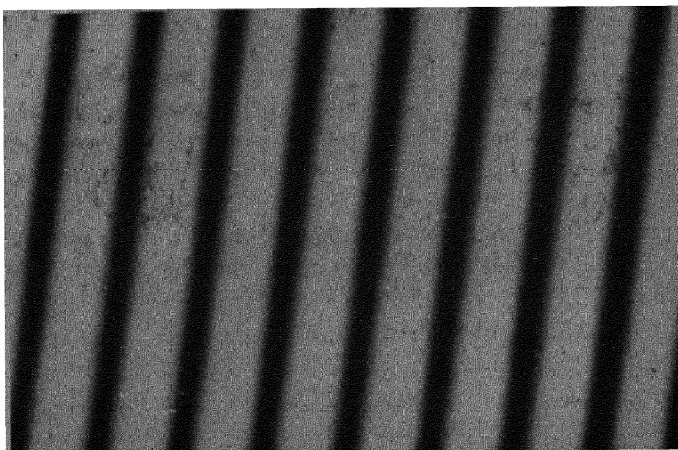


Fig. 9.—One of the preliminary masks used in the photographic method of synthesizing electron density projections.

(blackening) is approximately proportional to the projected electron density. Atoms show up as regions of high density. The picture thus looks like an actual photograph of the unit cell. (This procedure gives a *square* picture of the unit. If the actual projection is not square, a picture of the correct shape can readily be obtained by rephotographing the square picture, tilted approximately.)

Figure 10 shows a photographic projection of a simple structure (fluorite, CaF_2) made in this way with a preliminary set of masks. A more accurate and more extensive set of masks, which should prove useful in the analysis of much more complex structures, has recently been made. A photographic projection of a molecule of the dye phthalocyanine obtained with this new set is shown in Figure 38 on page 67. Although there is still much room for improvement, this procedure, even in its present form, gives

the closest approach to direct photography of atoms and molecules yet attained.

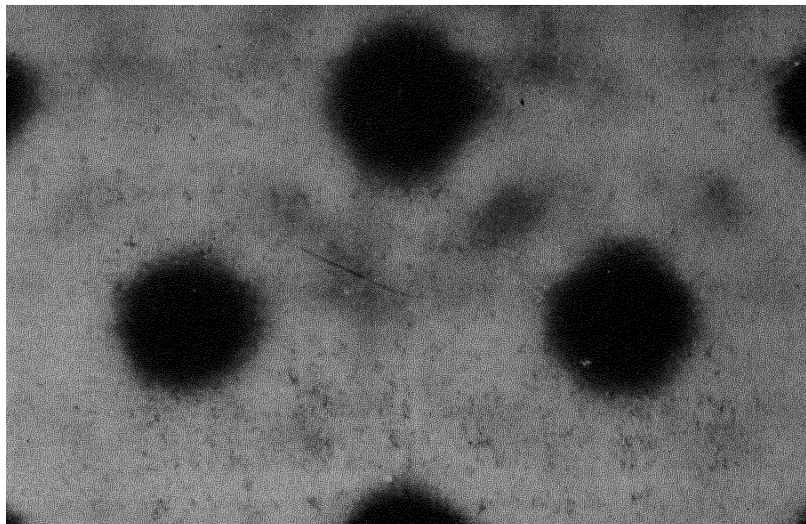


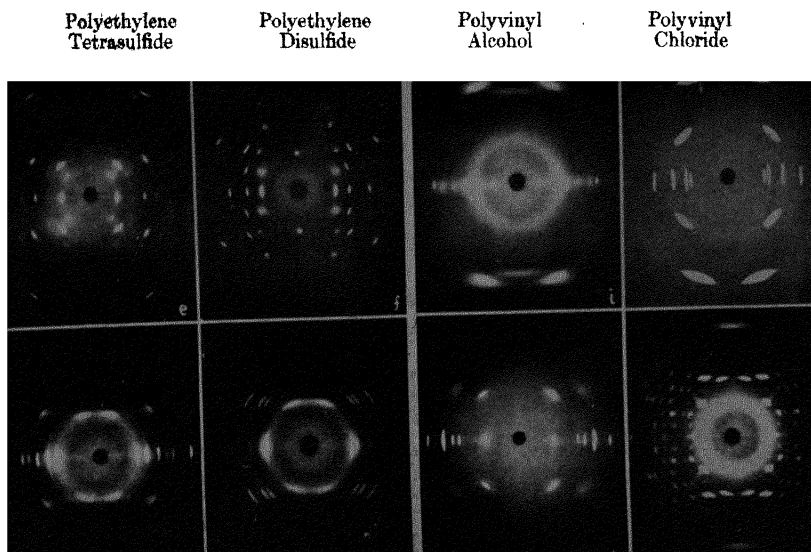
Fig. 10.—Electron density projection of a portion of the unit cell of calcium fluoride, from x-ray data by Havighurst (8).

IV. APPLICATIONS OTHER THAN STRUCTURE DETERMINATION

The greatest and most important use of x-ray diffraction data is for crystal-structure determination. Nevertheless, such data have proved, and will continue to prove, useful for other purposes.

One obvious use is to determine whether a given sample is crystalline or amorphous or is a material containing both crystalline and amorphous regions (see Fig. 11). A change in the degree of crystallinity (*e. g.*, on annealing a metal) or of relative orientation of the component molecules (*e. g.*, on stretching a sample of a substance composed of chain molecules) can be followed by noting the appearance or disappearance of x-ray diffraction effects (Figs. 12 and 13).

If the crystals or crystalline regions in a semicrystalline sample are very small (for example, less than 100 times the average distance between atoms), x-ray diffraction "lines," which would be very narrow for larger crystals, are broadened. Attempts have been made to estimate the average "crystallite" size from the degree of broadening. Most of these esti-

 β -Gutta Percha

Polychloroprene

Polyvinylidene
Chloride

Polyisobutylene

Fig. 11.—X-ray diffraction photographs (9) of synthetic polymers and gutta-percha, partially oriented by stretching or cold drawing. Some of the spots have been "touched up" to make them more evident in the reproduction.

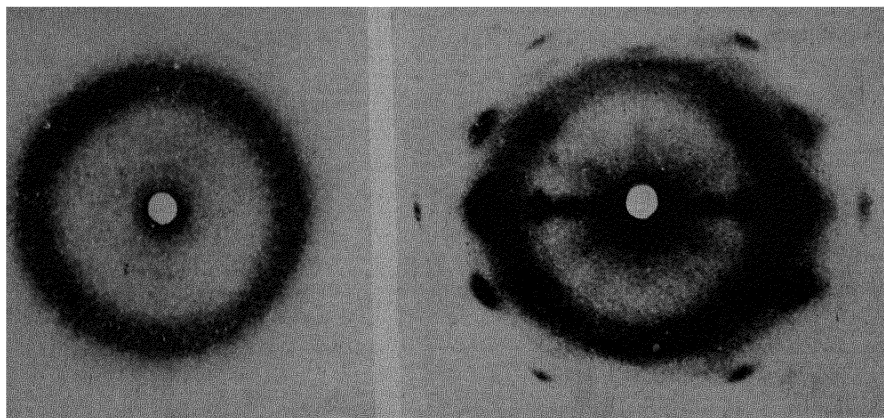


Fig. 12.—Rubber (10): (a) unstretched; (b) stretched.

mates mean little; however, since irregularity of structure also produces broadening of the lines.

The orientation of the internal structure of a crystal can readily be determined, for example, from a Laue photograph. This technique is of value in connection with the cutting of quartz crystals for radio frequency control. The approximate degree of orientation and the predominant direction of orientation of "crystallites" in films and fibers composed of (natural or synthetic) chain molecules are important commercially; they can simply and readily be deduced from x-ray diffraction photographs.

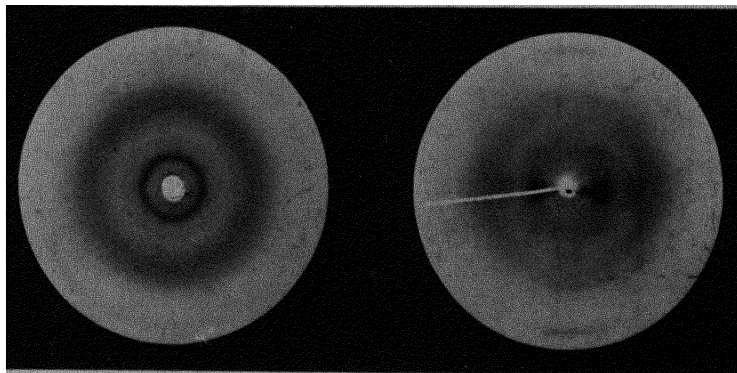


Fig. 13.—Gelatin: left, unoriented; right, oriented by stretching. (Courtesy of R. L. Griffith.)

Another highly important field of usefulness of x-ray diffraction data is that of the *identification* of crystalline substances. Identification is most simply accomplished by means of powder photographs (Fig. 7). The powder diffraction pattern serves as a fingerprint, characteristic of the crystalline species present. (Graphite and diamond; different forms of carbon, give different patterns.) Powder mixtures give patterns showing the lines characteristic of all the constituents.

To facilitate the use of powder diffraction data for identification, a card index containing pertinent data for a large number of crystalline substances is now available.*

* This card index project, initiated by the National Research Council Committee on X-Ray and Electron Diffraction, is being continued by cooperation between the American Society for X-Ray and Electron Diffraction, and American Society for Testing Materials, and the Institute of Physics (of Great Britain). Distribution of the card indices is handled by the American Society for Testing Materials, 260 South Broad St., Philadelphia, Pa.

X-ray identification methods are of great value in studies of metal and alloy systems. Crystalline components, solid solutions, eutectic mixtures,

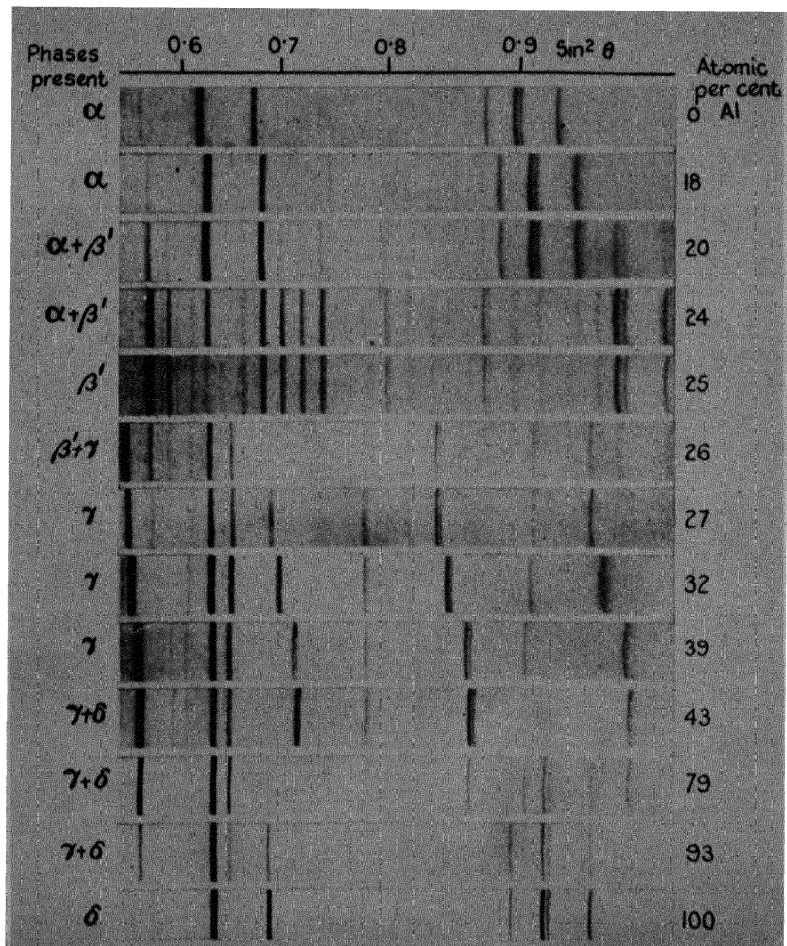


Fig. 14.—Powder photographs (11) showing changes of structure in the silver-aluminum system.

etc., are readily detected and identified, both at room temperature and, with the aid of special high-temperature diffraction cameras, at elevated temperatures (Fig. 14).

V. THE STRUCTURES OF TYPICAL ELEMENTS

In the remainder of this chapter, typical examples of results of crystal structure analysis by x-ray diffraction methods will be considered. The structures of some of the elements will be considered first.

The structures of the more electronegative elements—those placed on the right-hand side of the periodic table—are best interpreted in terms of the

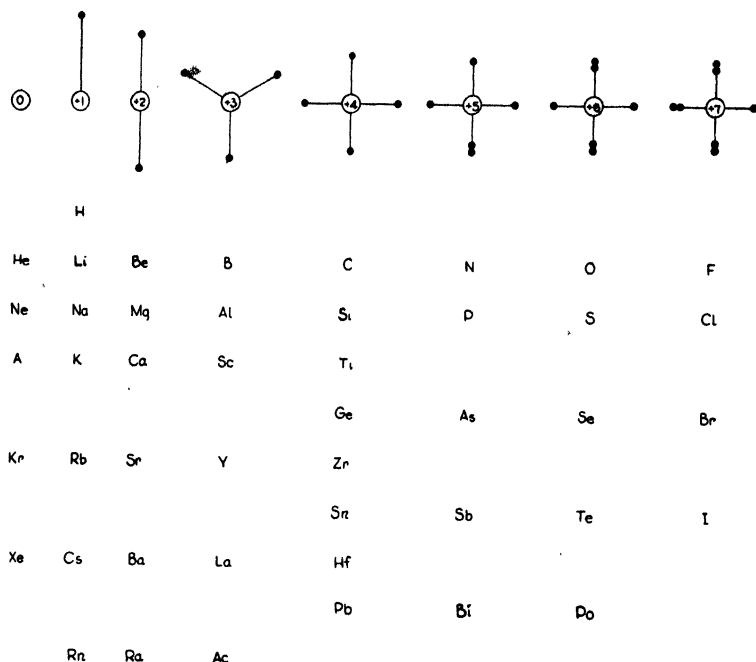


Fig. 15.—Relationship between atomic structures and the periodic table, according to the Lewis theory of valence.

Lewis theory of valence (12, 13). According to this theory, an isolated neutral (uncharged) atom of one of these elements possesses a number of valence electrons equal to the number of the column of the periodic table in which that element belongs (Fig. 15). Atoms tend to share valence electrons, in pairs, until each has a valence shell of a type which is especially stable. The most common stable valence shell consists of four electron pairs tetrahedrally oriented. (The electrons are presumed to be in constant motion in orbits which have a certain preferred orientation. If an

electron pair is shared by two atoms, the orbits of the two electrons of the pair enclose both atomic kernels.)

According to this theory, halogen atoms, each having (when isolated) seven valence electrons, combine to form diatomic molecules (F_2 , Cl_2 , etc.), in order that, by sharing an electron pair, each atom may have a stable valence shell of four electron pairs:



The stable existence of diatomic halogen molecules is, of course, well known from chemical evidence, measurements of gas densities, etc. It has also been confirmed by electron diffraction and band spectrum studies of the gases and by x-ray diffraction studies of the solids.

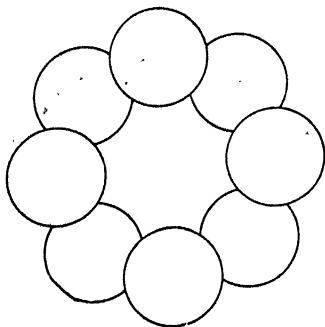


Fig. 16a.—The structure of a single molecule of rhombic sulfur, according to Warren and Burwell (14).

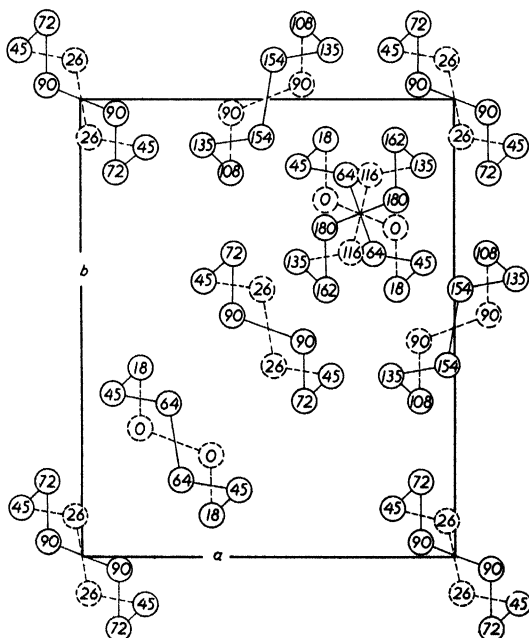


Fig. 16b.—Distribution of molecules of sulfur in the unit cell (14).

The elements in column 6 of the periodic table have six valence electrons each. Oxygen forms diatomic molecules with a peculiar structure which need not be discussed here. Sulfur, selenium and tellurium, as would be expected from the Lewis theory, form molecules in which each atom is bonded by shared electron pairs to two others. This results in ring molecules (*e. g.*, S_8 , Figs. 16a and 16b) or in *giant chain molecules* (Fig. 17).

Rubber-like, amorphous sulfur contains long flexible chains, probably with rings of various sizes in addition. The rubber-like elasticity results from the tendency of the flexible chains—having more or less free rotation about each S—S bond—to assume a kinked configuration rather than an extended one.

Nitrogen, in column 5 of the periodic table, forms diatomic molecules containing a triple bond (Fig. 18). [For reasons which we cannot discuss here because of limitations of space, double and triple bonds between elements other than those in the top

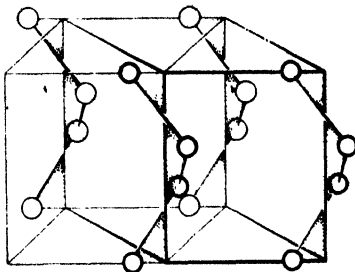


Fig. 17.—The structure of one crystal form of selenium (or tellurium) (18). The spiral chains extend completely through the crystal. The distribution of chain axes is that shown in Figure 33a.

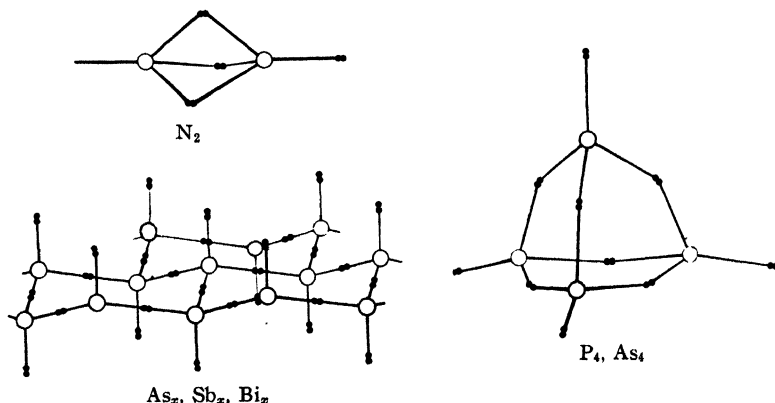


Fig. 18.—Representing the structures of N_2 , P_4 , As_4 and $As_2Sb_2Bi_2$ molecules.

row of the periodic table—O, N, C, and perhaps B—are rare and relatively unstable (12).] Phosphorus and arsenic form tetrahedral tetratomic molecules in which each atom is bonded to three others (15–17). Phosphorus.

arsenic, antimony and bismuth also form *giant layer molecules*, in which each atom is bonded to three others (13, 18, 19).

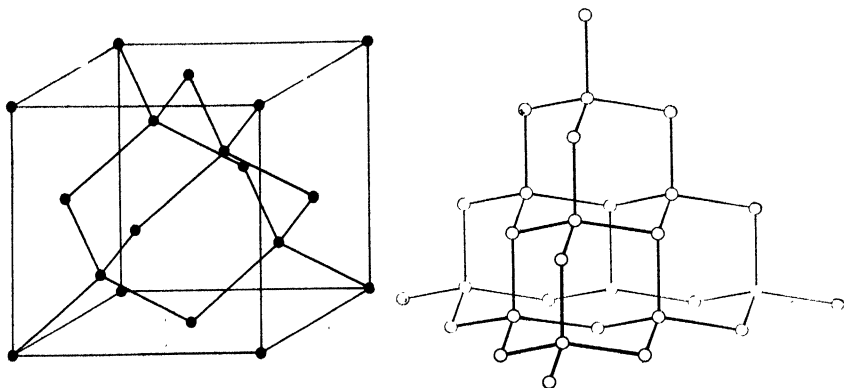


Fig. 19.—The structure of C (diamond), Si, Ge and Sn (gray): left: the unit cube; right: a portion of the structure, from another viewpoint.

Carbon, silicon, germanium and tin, in column 4 of the periodic table, have four valence electrons per atom. Each of these elements forms crys-

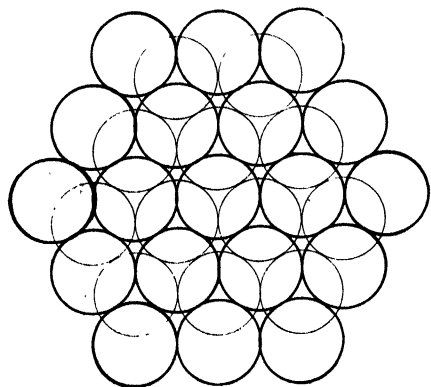


Fig. 20.—Illustrating the close packing of spheres.

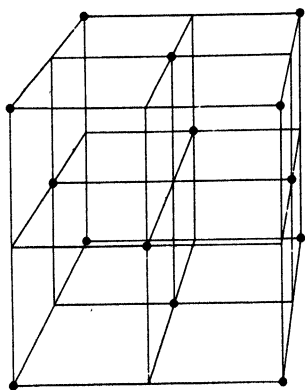


Fig. 21.—Unit cube of the face-centered cubic structure, also known as “cubic close packing.” Many metals have this structure (18).

tals in which every atom is bonded to four others, tetrahedrally around it (13, 18) (Fig. 19). Each crystal is a single *giant network molecule*.

There is no way in which atoms of elements with less than 4 valence electrons per atom can complete tetrahedral 4-electron-pair valence shells by sharing electron pairs with other atoms. Most of the more metallic elements form crystal structures of one of the *close-packed* types, in which each atom is surrounded by the maximum possible number (twelve) of near-neighbors (Figs. 20 and 21). The valence electrons are relatively free to move between the atoms. This easy motion is responsible for metallic conduction.

VI. THE STRUCTURES OF SOME SIMPLE INORGANIC COMPOUNDS

When two atoms of different elements share an electron pair between them, that pair is not, in general, shared equally. One atom holds the elec-

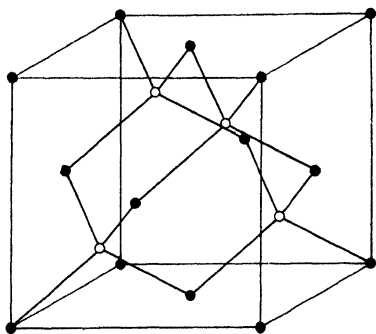


Fig. 22.—Unit cube of cubic ZnS structure. Among the compounds (18) which have this structure are: CuF, CuCl, CuBr, CuI, AgI, BeS, ZnS, CdS, HgS, BeSe, BeTe, AlF, SiC.

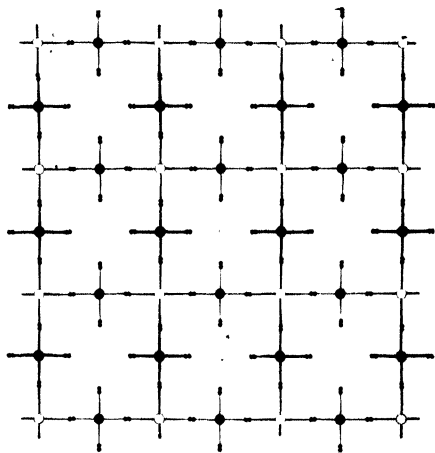


Fig. 23.—Distribution of atomic kernels and valence electrons in a portion of a layer molecule of mercuric iodide, HgI_2 (20).

tron pair more tightly than the other; the bond has polarity. The structures of typical compounds in which the atoms are connected by partially polar electron pair bonds are depicted in Figures 22, 23 and 24.

The structure of Figure 22 is like that of the diamond (Fig. 19) except that the atoms are of two kinds and the valence electron pairs are unequally shared. All of the compounds known to have this type of structure have an average of four valence electrons per atom, just the number required for a pair between each pair of adjacent atoms (13).

Figure 23 shows the atomic distribution in a portion of a single giant layer molecule, of which a mercuric iodide crystal is composed (20). Each

mercury atom is tetrahedrally bonded to four iodine atoms. Each iodine atom also has a tetrahedral 4-electron-pair valence shell, two of the four pairs being shared with neighboring mercury atoms.

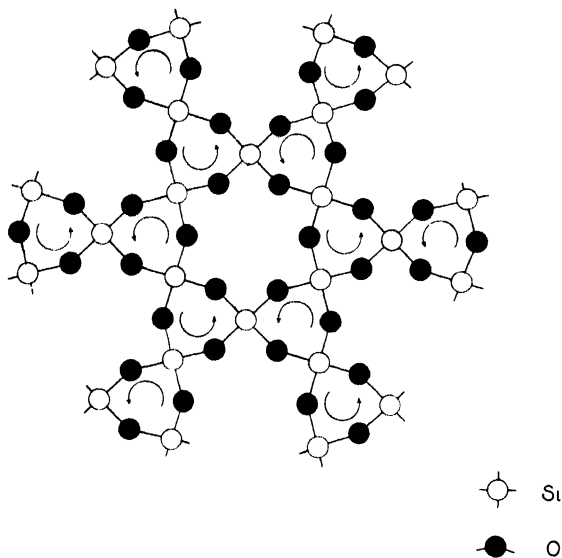


Fig. 24.—A projection of a portion of the quartz (SiO_2) structure.

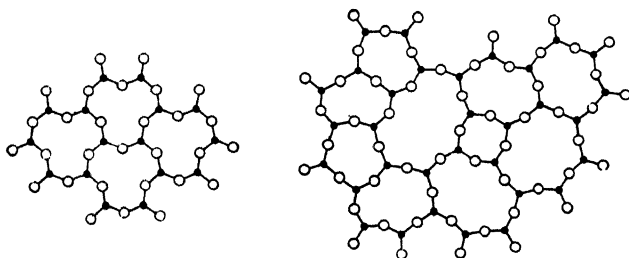


Fig. 25.—Schematic representation after Zachariasen (21) and Warren (22) of the difference between the structure of (left) crystalline silica (*e. g.*, quartz) and (right) vitreous silica. For simplicity of representation, the coordination number of Si is here assumed to be 3, rather than 4, its true value.

The quartz (SiO_2) structure, shown in projection in Figure 24, is like that of mercuric iodide, as regards the arrangement of the more electronegative atoms (O, I) immediately around each electropositive atom

(Si, Hg), and vice versa, but the relative positions of more distant atoms differ in the two structures (13, 18). In quartz, the whole crystal is a single giant network molecule.

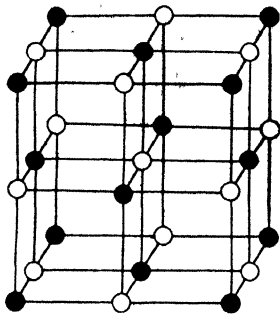


Fig. 26.—Unit cube of sodium chloride structure. Among the compounds (18) which have this structure are: LiX (X = F, Cl, Br or I), NaX, KX, RbX, CaF₂, AgF, AgCl, AgBr, MgO, CaO, SrO, BaO, MgS, MgSe, CaTe, ScN, TiC.

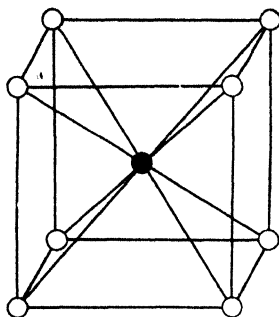


Fig. 27.—Unit cube of the cesium chloride (CsCl) structure. Among the compounds (18) which have this structure are: CsCl, CsBr, CsI, TlCl, TlBr, TlI.

It may be noted parenthetically that in vitreous silica (silica glass) there is a similar distribution of four oxygens around each silicon and two silicons around each oxygen. Long-distance regularity is lacking, however (see Fig. 25).

In a compound composed of two elements which differ greatly in electronegativity (*i. e.*, in the attraction of the atomic kernels for valence electrons), all of the valence electrons may be held by the more electronegative atoms. The crystal is then an assemblage of the charged ions so produced. In all such crystals, each negative ion is surrounded by positive ions and each positive ion has only negative ions as close neighbors. The formula of the compound depends on the relative numbers of ions of the

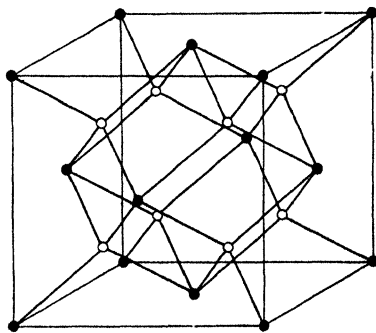


Fig. 28.—Unit cube of the calcium fluoride (CaF₂) structure. Among the compounds (18) which have this structure are: CaF₂, SrF₂, SrCl₂, BaF₂, CuF₂, CdF₂, CeO₂, ZrO₂, Li₂O, Li₂S, Li₂Se, Li₂Te, Na₂O, Na₂S, K₂O, K₂S, Cu₂S, Mg₂Si, Mg₂Sn, Be₂C.

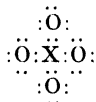
two kinds necessary for electrical neutrality, and therefore on the ionic charges.

Figures 26, 27 and 28 represent the crystal structures of typical simple ionic compounds. In the NaCl-type structure (Fig. 26), each ion has six of the other kind around it. In the CsCl structure (Fig. 27), the *coordination number* of each ion is 8. In CaF₂ (Fig. 28), the coordination numbers of the calcium and fluoride ions are 8 and 4, respectively.

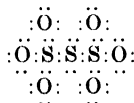
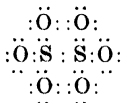
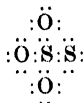
VII. THE STRUCTURES OF SOME MORE COMPLEX INORGANIC COMPOUNDS

Of the many more complex inorganic compounds whose crystal structures (18) have been determined, only a few will be mentioned here.

The structures of salts containing polyatomic ions show that most of these ions have the structures to be expected from the Lewis theory (12). For example, the perchlorate, sulfate, orthophosphate, and orthosilicate ions are all tetrahedral, conforming to the following "dot formula" (indicating the valence electron distribution).



The structures of the thiosulfate, dithionate and trithionate ions are in agreement with these dot formulas:



In the complex amines, with which Werner's name is usually associated, the NH₃ groups are bonded, through the nitrogen, to the central metal atom (12, 23). The "lone pair" of the nitrogen in the ammonia molecule



has thus become a bonding pair. Likewise, in the formation of the complex cyanide ions, *e. g.*, Fe(CN)₆⁻⁴, a lone pair in each cyanide ion becomes a bonding pair, holding this group to the central metal (Fe) atom.

Most of the complex silicates can be considered as aggregates of giant negatively charged silicate ions, Si₂O₇⁻², and small positive ions, Na⁺, Ca⁺⁺, etc. In the silicate ions, each silicon is bonded to four oxygen atoms (as in quartz), and each oxygen is bonded to either one or two silicon atoms.

In some minerals, the silicate ions are chains extending through the crystal; in others they are giant layer ions; while in still others the crystal consists of a single giant network ion with small positive ions interspersed within it (Figs. 29 and 30).

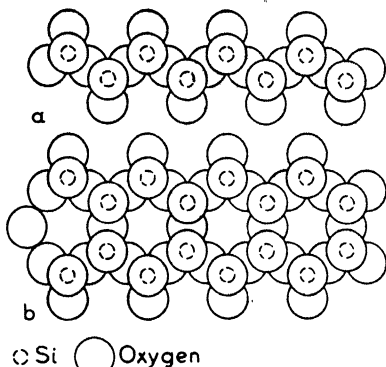


Fig. 29.—Sections (24) of giant silicate chain ions, in pyroxenes (a) and amphiboles (b).

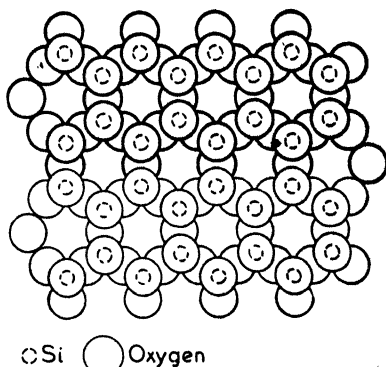


Fig. 30.—A portion of a giant silicate layer ion in mica (24).

VIII. THE STRUCTURES OF SOME ORGANIC COMPOUNDS

A large number of organic crystal structures has also been studied by x-ray diffraction methods. A few of these will now be briefly discussed.

In iodoform, CHI_3 (25), as would be expected, the atoms are grouped together in molecular units (Fig. 31). Each carbon-hydrogen bond is on a threefold symmetry axis. The molecules are so placed and oriented as to give approximate close packing of molecules, considered as units, and also of iodine atoms, considered separately. Each hydrogen atom is surrounded by three iodine atoms of neighboring molecules.

Normal paraffin hydrocarbons crystallize with the molecules in extended zigzag chains (Fig. 32), with the chain axes parallel to each other. The arrangement of the chains departs somewhat from the close-packed arrangement to be expected if they were truly cylindrical (Fig. 33).

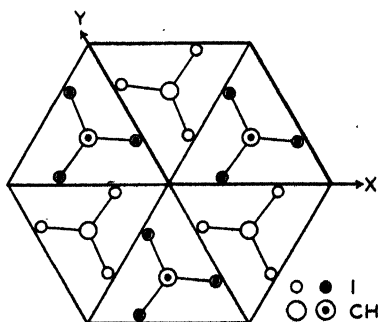


Fig. 31.—Projection of portion of structure of iodoform, CHI_3 (25).

Many simple derivatives of normal paraffin hydrocarbons also crystallize with their chain axes mutually parallel. The atomic distribution in a crys-

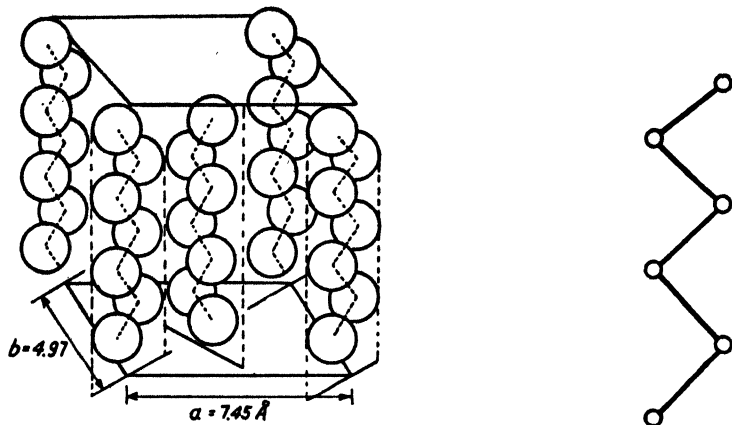


Fig. 32.—Arrangement of carbon atoms in a normal paraffin hydrocarbon crystal (26).

tal of a straight-chain alcohol, for example, is schematically represented in Figure 34. The alcohol molecules line up head-to-head in such a way as to give *hydrogen bridges* between the oxygen atoms of neighboring molecules.

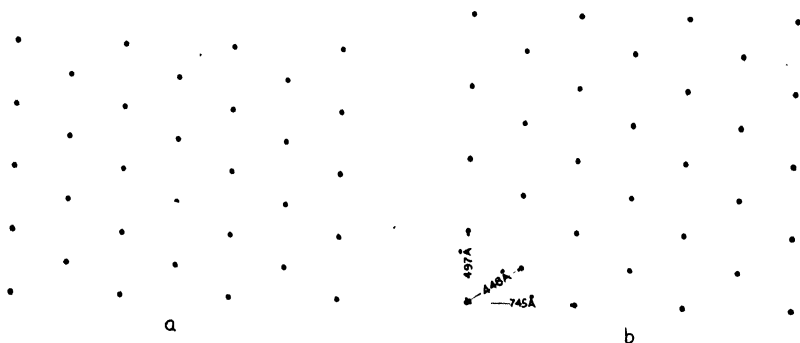


Fig. 33.—Distribution of molecular axes in (a) a close-packed assemblage of cylindrical molecules, and (b) a normal paraffin crystal.

The structure of polyvinyl alcohol (Fig. 35) is interesting. Here again there are parallel zigzag chains, with adjacent molecules connected by means of hydrogen bridges.

Figure 36 shows a contour map, representing the electron density projection of the structure of oxalic acid dihydrate, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, with a diagram showing the distribution of atoms deduced from this projection (and other

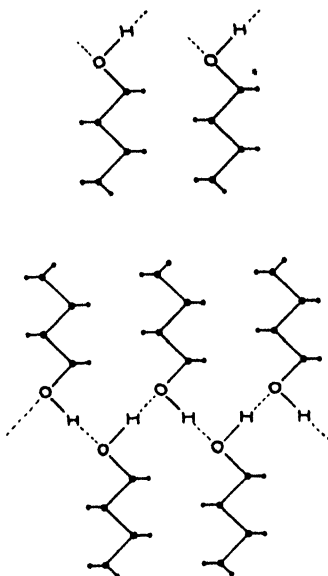


Fig. 34.—Schematic representation of crystal structures of normal alcohols (27).

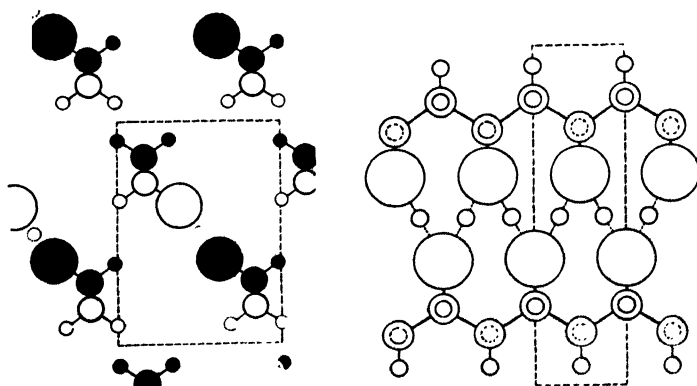


Fig. 35.—The structure of polyvinyl alcohol (28).

data). The dotted lines show the location of hydrogen bridges connecting the water (or H_3O^+) oxygen atoms with the carboxyl oxygen atoms.

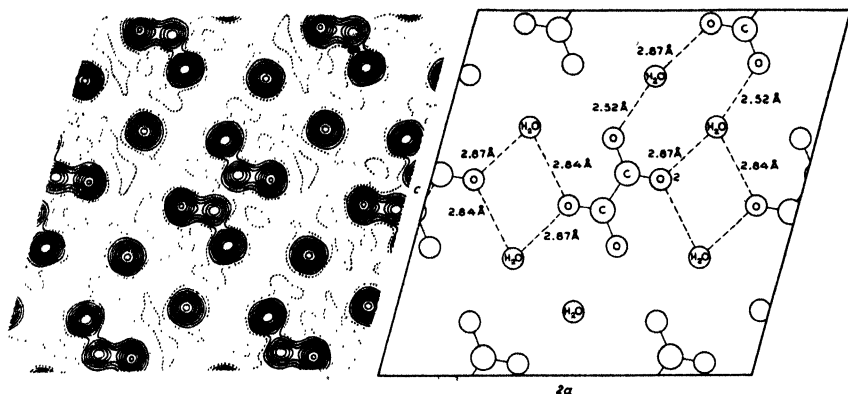


Fig. 36.—The structure (29) of oxalic acid dihydrate, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ or $(\text{H}_3\text{O})_2\text{C}_2\text{O}_4$.

A contour map representing the electron density projection of the structure of phthalocyanine is shown, with the molecular formula, in Figure 37. The corresponding photographic projection, made with the author's set of

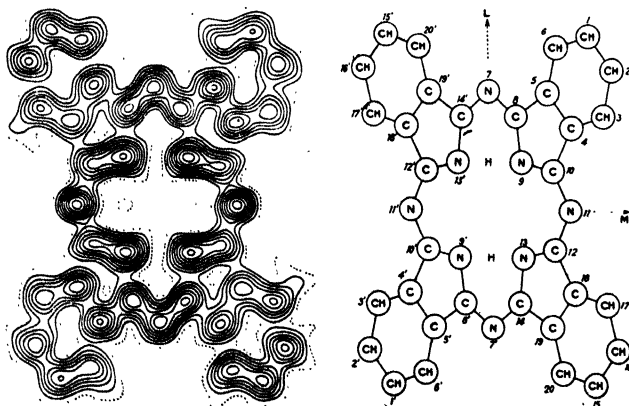


Fig. 37.—The structure of phthalocyanine (30).

masks, using the same x-ray data, is shown in Figure 38. This structure contains two of the relatively rare NHN hydrogen bridges. The two hydrogens of these bridges may be replaced by a metallic atom, such as Be

or Ni, which occupies a position in the center of the whole, bonded to the four close nitrogen atoms.

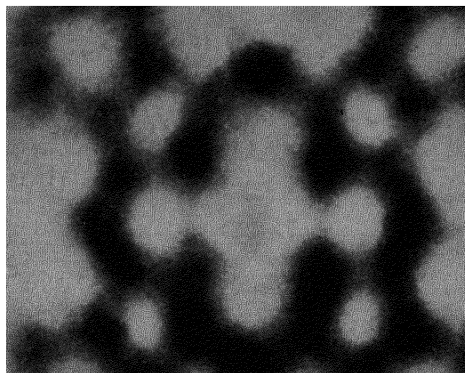


Fig. 38.—Photographic projection of the structure of phthalocyanine, using x-ray data by Robertson (30).

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IV. *Chemical Spectroscopy*

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T

HE APPLICATION OF SPECTROSCOPIC METHODS to chemical analysis (1-6) can be easily divided into the methods which deal with emission spectra of elements and their qualitative and quantitative analysis and those which deal with the absorption spectra of combinations of elements (see Chapter V). Before presenting either of these topics, a brief summary of the theory and nomenclature involved will be discussed.

I. RADIANT ENERGY

The accepted theories of light and radiant energy involve a wavelike propagation, capable of reflection, interference, retardation and refraction.

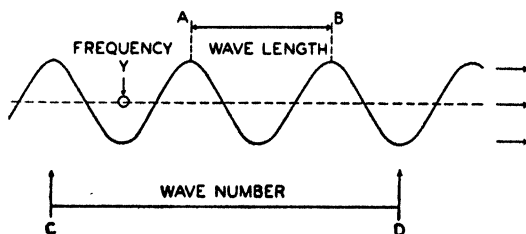


Fig. 1.—Graphic indication of the relation between wave length (λ), wave number (ν'), and frequency (ν).

Graphically, the wave form may be represented as shown in Figure 1, in which the distance between nodes in the wave form is known as the wave length (λ), the number of these nodes in a given unit of distance (meter,

inch, etc.) is known as the wave number (ν'), and the number of the nodes which pass a fixed point in a unit period of time (second) is known as the frequency (ν). The relation between these three units may be expressed as:

$$1/\lambda = \nu' = \nu/c$$

where c represents the speed of light in the medium through which the radiant energy passes. For exact correction of data, due consideration must be given to the medium, temperature and pressure, but for most work in chemical spectroscopy it is sufficient to consider c as approximately 3×10^8 meters per second.

The ordered distribution of radiant energy in accordance with its wave length or frequency results in a spectrum; hence, this becomes the definition of a spectrum. While we use the terms "light" and "radiant energy" somewhat interchangeably, it should be remembered that the visible portion of the spectrum, which is the spectral region generally known as light, involves only a small portion of the total range of radiant energy. The visible region in terms of wave length extends from 4×10^{-7} to 7.5×10^{-7} meters. The accuracy with which the earlier workers could determine wave length values within this region justified the use of a number with four significant figures in front of the decimal point, so that the limits of the visible spectrum might thus be indicated as from 4000×10^{-10} to 7500×10^{-10} meters. The unit of measurement in this system was called an ångström, after the Swedish physicist Ångström, and is now defined as $1/6438.4696$ of the wave length of the cadmium red line, rather than one ten thousand millionth ($1/10,000,000,000$) of a meter. The increase in accuracy of modern physical methods has enabled us to measure wave length values to an accuracy of one part in about ten million, or to about four significant figures after the decimal point in the ångström system of notation.

In much of the data published on absorption spectra of organic compounds and in studies on visible color, the accuracy of the spectral measurements does not justify more than three significant figures, and in the infrared region the wave length value increases to such a size that ångström values are awkward to use. A variety of wave length, wave number and frequency units have therefore been used, depending on the spectral region and the data considered. For reasons which will be discussed in the second of these two lectures (Chapter V), the use of frequency or wave number values rather than wave length is found to be more convenient in certain forms of absorption spectra data. The more commonly accepted units

used in the spectral regions available to the chemical spectrographer (2000 to 15,000 Å) are indicated in Table I (Fig. 2).

TABLE I

DEFINITION OF IMPORTANT RADIANT ENERGY UNITS USED IN CHEMICAL SPECTROSCOPY

<i>Wave length, λ</i>		
Angström, Å (among other symbols that have been used for this term are IA, A, and AU)	=	$1/6438.4696$ of the wave length of the Cd red line = meters $\times 10^{-10}$
Millimicron, $m\mu$	=	meters $\times 10^{-9}$
Micron, μ	=	meters $\times 10^{-6}$
<i>Wave number, ν'</i>		
Waves per centimeter	=	cm.^{-1}
<i>Frequency, ν</i>		
Fresnel, f	=	vibrations per (second $\times 10^{-12}$)

In this chapter we shall not discuss in detail the equipment essential to chemical spectroscopy, but rather the principles involved and their applica-

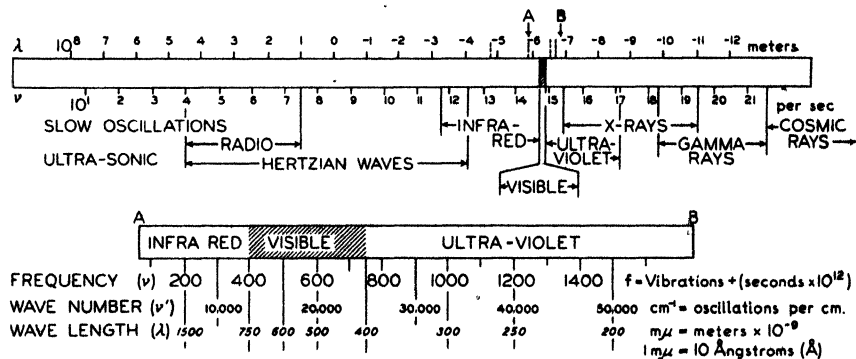


Fig. 2.—Spectral distribution of radiant energy.

tion to chemical problems. The chemist should have some knowledge of the physical principles involved in the equipment he is using; but for many determinations, such as refractometry, polarimetry and spectrometry, he should be more concerned with the interpretation of the data. In Figure 3 is shown the schematic diagram of a spectrograph and in Figure 4, a spectrogram obtained from a spectrograph. It should be noted that the lines in the spectrogram are in reality photographs of the slit which has been illuminated by a heterogeneous light source composed

of discrete wave length regions and that in the optical system of the spectrograph there is both a focusing device (lenses) and a refracting device (prism) which separates the discrete wave length regions in accordance with their numerical wave length values.

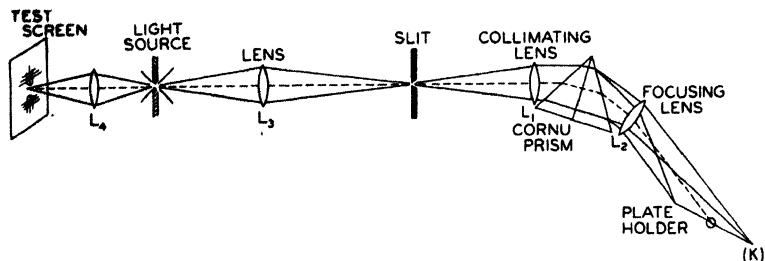


Fig. 3.—Optical diagram of a spectrograph.

In addition to the use of a prism as the refracting and dispersing medium, we may also use a ruled grating. The type and size of instrument used will depend on the nature of the problem and the availability of equipment.

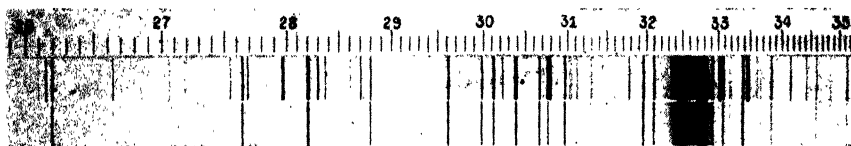


Fig. 4.—Spectrograms of brass (top) and copper (bottom).

The wide variety of instruments in size and optical principle prevents to some extent the more universal application of certain analytical methods, as will be pointed out in our subsequent discussion.

II. CHEMICAL ANALYSIS BY EMISSION SPECTRA

1. Emission Spectra

This lecture and the series of lectures of which this is a part have been arranged in the interest of providing information on the practical applications of physical methods to chemical problems. Hence, no elaborate discussion can be included of the theoretical aspects of emission spectra, nor is any comprehensive knowledge of this field necessary for an appreciation and understanding of the uses of spectroscopic methods of analysis. It will be necessary to accept certain information without a complete explanation of the theoretical basis.

Our concept of atomic structure involves a central positive nucleus in the atom surrounded by a number of negative electrons. The number of negative electrons and the size of the positive nucleus determine the element. The arrangement and number of negative electrons conform to certain principles and rules which have been elaborately developed and proved through theoretical and experimental work.

Among the fundamental concepts is the existence of certain levels or shells surrounding the central nucleus which the electron may populate. The movement of an electron to outer shells or levels will require energy, and the falling back of the electron to lower or inner levels will result in the emission of energy. The energy required for the pushing out of an electron to higher levels may be applied to the atom in the form of heat, electrical force or light. In the latter case, we have absorption of light of a frequency corresponding to the energy required for the electron shift.

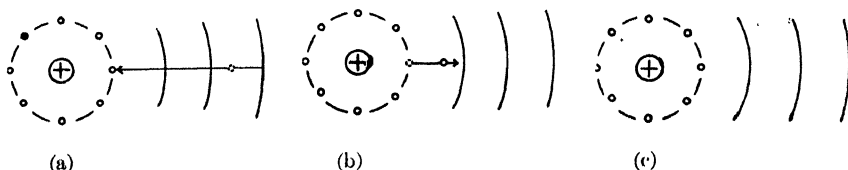


Fig. 5.—Qualitative representation of (a) emission, (b) absorption and (c) normal state (7).

The return of the electron to lower levels results in emission of energy, an emission usually in the form of light or radiant energy of a frequency corresponding to the energy evolved. This electron shifting can be depicted schematically as indicated in Figure 5. The energy values for such an electron shift can be plotted with respect to the level occupied and distance traveled by the electron (Fig. 6). This graphical indication of energy values is based on the various levels occupied by a single electron after it is pushed out from or drops back into a configuration in which all other electrons in the atom are at their lowest or ground state. It will be noted that, as the electron is removed further and further from the central or positive nucleus, the energy spacing between levels decreases, so that at a finite energy value the electron can be removed from the sphere of influence of the remainder of the atom, a condition which is often referred to as ionization. This ionized atom will then have an outer electron configuration of the next lower element in the periodic table, but a positive charge on the center which remains as before. For example.

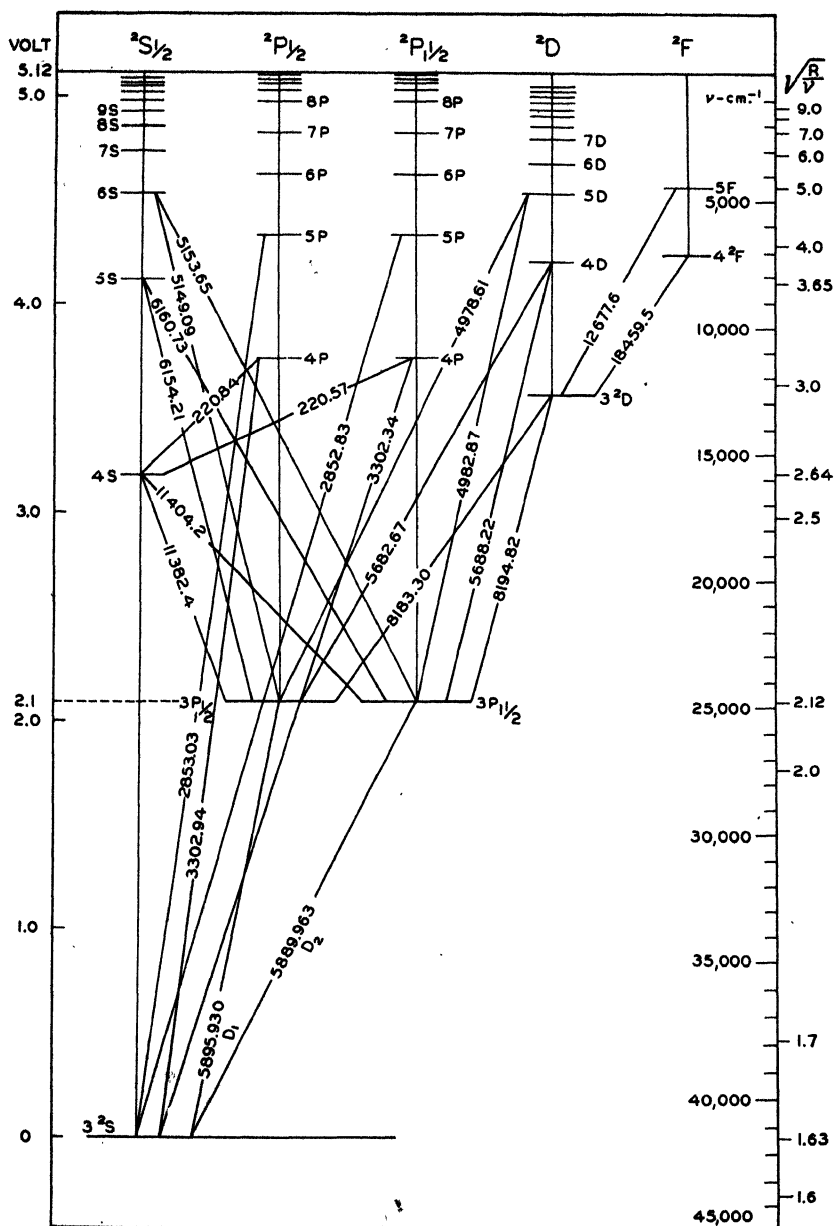


Fig. 6.—Level diagram of sodium.

the removal of an electron from the aluminum atom gives a charged magnesium-like electronic configuration (Fig. 7).

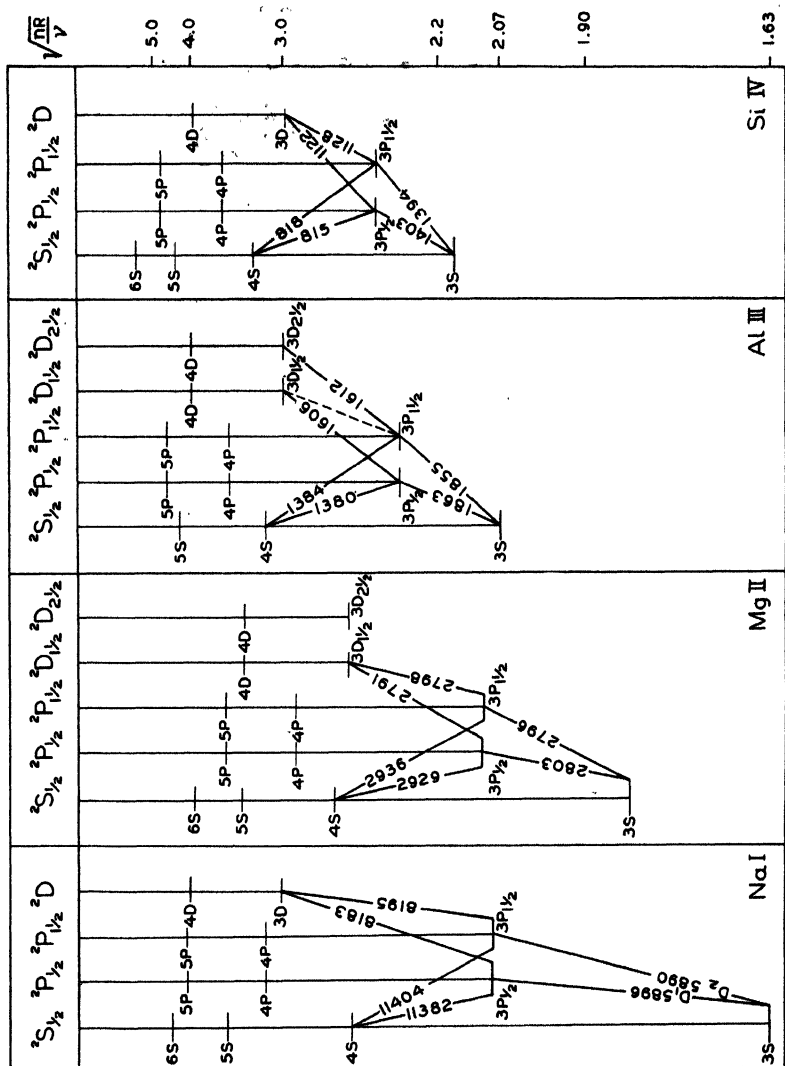


Fig. 7.—Level diagrams of four spectra arising in a system of 11 electrons, each system having a different ionization potential (∞ S) for Na = 5.12, Mg II = 15, Al III = 28.3, and Si IV = 44.95 v.

2. Qualitative Analysis

The similarity in electronic structure of partially ionized atoms to the electronic structure of atoms of other elements with lesser or higher degrees

of ionization results in similarity of resulting spectra. It thus becomes possible to predict the degree of ionization of an atom from the characteristics of the spectra produced (Fig. 7). In low-temperature arcs and flames, it is expected that the majority of the spectra produced will be those of the first stage of ionization, *i. e.*, the spectra resulting from the falling into normal position of the first electron to be pushed out. Such spectra are usually indicated by the designation I, and higher degrees of ionization by the designations II, III, etc. These higher states of

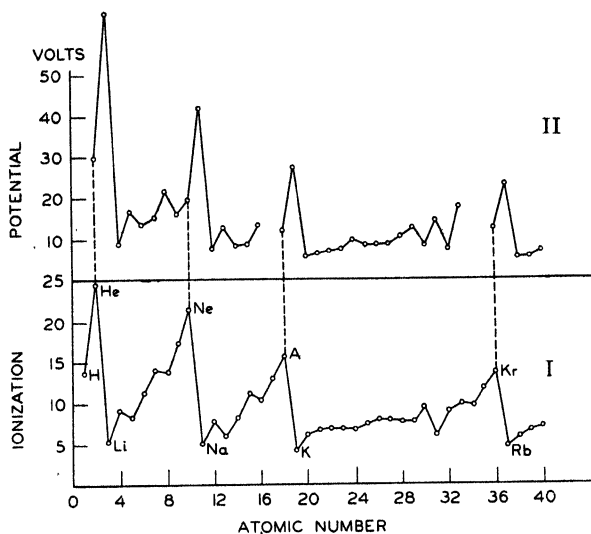


Fig. 8.—Ionization potential of some of the elements (I) (lower) and ionization potential of these singly ionized elements to doubly ionized elements (II) (upper). Note that, in the II series, zero voltage for each element is its single-ionization potential.

ionization are generally produced by spark or other high-temperature or high-voltage forces (Fig. 8).

There are a number of definite rules governing the particular transitions between levels that are possible in the production of spectra, and hence we may expect and will find that each element produces definite spectra which often makes possible its identification in a spectrum of several elements by simple visual observation of the negative. Certain elements may have groups of lines which repeat at regular intervals, such as combinations of doublets, triplets, quadruplets, etc. The triplet combinations of manganese, the doublet combinations of aluminum and

sodium, and the quintuplet combinations of magnesium are examples of such easily identified arrangements (Fig. 9).

The characteristic and almost fingerprint-like identification exhibited by many of the elements in their spectra provides a positive and sensitive method of rapid qualitative identification of elements in mixtures, especially where the element may be present in trace amounts. There are some elements, such as chlorine, bromine, oxygen, sulfur, etc., which do not readily yield spectra which can be used for qualitative identification, but about 70 of the 92 elements do yield satisfactory identification spectra. A disadvantage of spectral analysis is that it does not provide a means of indication of molecular combination or state of oxidation.

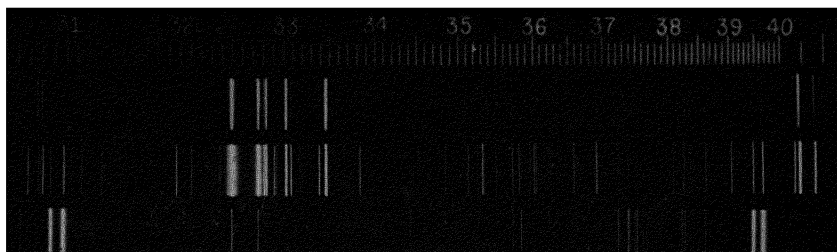


Fig. 9.—Spectrograms of two brass samples (top and middle) and of aluminum alloy (bottom).

The rapid qualitative analysis of mixtures does not require the identification of all of the spectrum lines in the spectrogram, but rather only a limited number of lines which have been selected for identification purposes. It has been shown experimentally that, as one dilutes an element in the unknown by some inert material, the intensity of the spectrum lines of the element under study becomes weaker, and eventually the lines of low intensity completely disappear when the exposure time is maintained at a constant value. The continuance of this dilution will reduce the number of lines of this element. The last lines to disappear are known as the persistent or ultimate lines of the element. The persistent lines for the elements which can be analyzed for by spectrographic methods have been determined, and in the qualitative analysis of a mixture one need only look for the persistent lines of an element to decide if the element is present. In order to avoid the possibility of confusion of weak lines of the principal component of the unknown with persistent lines of elements which may be present in trace amounts, it is essential that two or three

persistent lines be identified in order to confirm the positive presence of the trace element.

Tables of these persistent lines (also known as ultimate lines, *raies ultimes* or *letzten Linien*) have been prepared, an example of a portion of such a table being shown in Table II. Such tables can be arranged ac-

TABLE II

PORTION OF A PERSISTENT LINES TABLE ARRANGED ACCORDING TO WAVE LENGTH

Wave length, ångström	Element	Wave length, ångström	Element	Wave length, ångström	Element
3134.72	Hf II	3405.12	Co I	3642.78	Sc II
58.87	Ca II	06.66	Ta	46.20	Gd
63.40	Cb II	'14.77	Ni I	50.15	Hg I
'75.04	Sn I	21.24	Pd I	53.50	Ti I
79.33	Ca II	'34.89	Rh	54.83	Hg I
83.41	V II	36.74	Ru I	57.99	Rh I
83.98	V II	37.02	Ir I	63.28	Hg I
85.40	V II	38.23	Zr II	72.58	U
94.98	Cb II	51.41	B II	83.47	Pb I
3215.56	W I	'53.51	Co I	92.36	Rh I
'20.78	Ir I	60.47	Re I	92.65	Er

cording to element, for the purpose of rapid identification of the presence or absence of certain elements, or according to the wave length of lines observed for the purpose of identification of the unknown or trace elements. The absence of these persistent lines for any element indicates that the element is not present in a concentration detectable by the spectrographic method employed. The limit of detection is dependent on the intensity of the line chosen and will vary for different elements. In Table III it

TABLE III

MINIMUM CONCENTRATION FOR SPECTROGRAPHIC IDENTIFICATION OF ELEMENTS USING HILGER RU POWDER

0.000001 to 0.00001%	0.0001 to 0.001%
Ag, Co, Cr, Cu, In, Li, Mg, Na, Ni	B, Bi, Cd, Sb, Si, Zn, Zr
0.00001 to 0.0001%	0.001 to 0.01%
Al, Ba, Be, Ca, Fe, Hg, Mn, Mo, Pb, Sn, Ti	As, Cs, K, P, Rh

will be noted that the relative sensitivity for copper is far greater than that for boron, indicating that for very low concentrations the spectrographic method may not always be the most satisfactory or most sensitive one.

Each element produces a number of spectrum lines. These have been carefully measured and listed. The lists of spectrum lines may be ar-

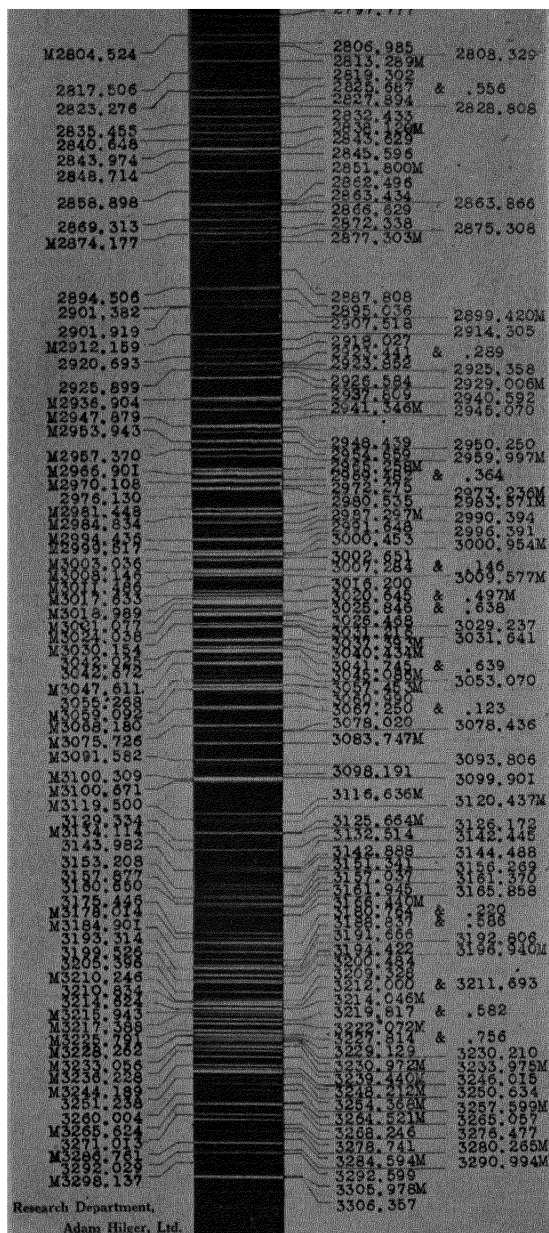
TABLE IV
PRINCIPAL LINES BY ELEMENTS
Aluminum

Wave length	Intensity		Wave length	Intensity	
	Arc	Spark		Arc	Spark
II 2 094.8	...	50	II 2 816.2	10	100
I 2 168.8	8R	12	3 050.1	18	10
I 2 174.0	8R	10	3 054.7	20	10
2 204.6	10R	10	3 057.2	15	18
I 2 210.0	12R	15	3 064.3	20	20
I 2 259.9	8	...	3 066.2	25	25
I 2 263.5	60R	25	I 3 082.2	800	800
I 2 269.1	60R	25	I 3 092.7	1000	1000
I 2 269.2	15R	...	3 092.8	50R	18
I 2 367.1	150R	50R	II 3 586.9	...	500
I 2 372.1	18	10	I 3 944.0	2000	1000
I 2 373.1	100R	30	I 3 961.5	3000	2000
I 2 373.4	200R	100R	II 4 962.1	15	3
I 2 378.4	40	20	I 5 557.0	15	...
2 568.0	200R	80R	I 5 557.9	15	...
2 575.1	200R	80R	II 6 231.8	...	30
2 575.4	30	30	II 6 243.4	...	100
I 2 652.5	150R	60	II 6 696.4	10	...
I 2 660.4	150R	60	6 698.8	10	...
II 2 669.2	3	100	7 836.9	15	...

TABLE V
PRINCIPAL LINES BY WAVE LENGTH^a

Wave length	Element	Intensities	
		Arc	Spark (discharge)
3233.24	W	2	9
3233.234	Cr I	30	4
3233.208	Ce	2	...
3233.190	V I	40	3
3233.174	Ni I	4	...
3233.154	Ag	...	10
3233.142	W II	2	6
3233.140	Mo	50	30
3233.11	Zr I	6	...
3233.054	Fe	100	60
3233.02	Ca	...	4
3232.963	Ni I	300R	35
3232.875	Ce	3	...
3232.874	Co I	60	25
3232.80	Kr I	...	(2)
3232.793	Cb	...	2h
3232.791	Ti I	8	...
3232.791	Fe II	...	50
3232.78	I	...	(5)
3232.751	Ru I	50	4

^a Portion of a page from Harrison, *M. I. T., Wavelength Tables of 100,000 Spectrum Lines*. Wiley, New York, 1939.



ranged in numerical order according to element, or in combination of all elements according to wave length or numerical order. In arrangement according to element, the data are useful in the elimination of lines to be identified where the element is the principal constituent, whereas the arrangement according to wave length is useful in the identification of lines of unknown origin (Tables IV and V).

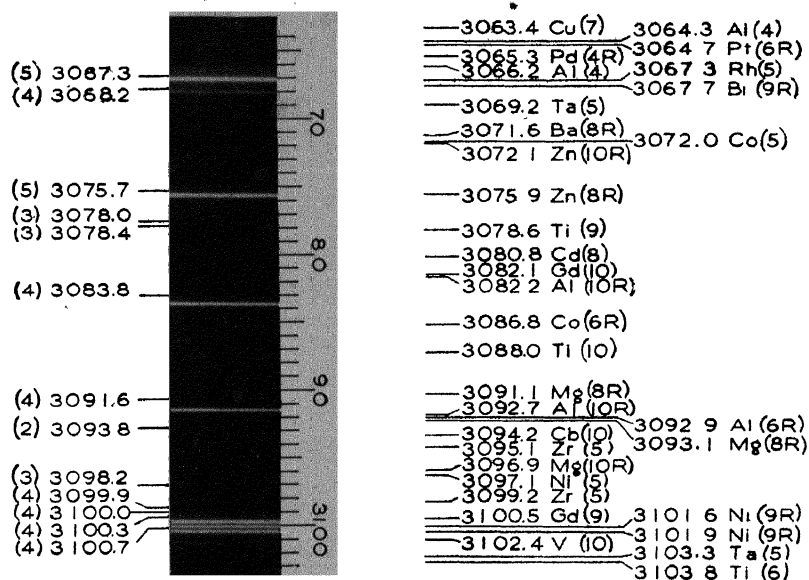


Fig. 11.—Chart for spectral analysis with iron comparison.

The determination of the wave length of spectrum lines is made through the means of accurate measuring machines with finely graduated scales. The accuracy required is such as to limit the availability of these instruments; it has been found that an inexpensive and highly accurate comparison scale can be applied to the spectrogram by photographing the spectrum of a known element adjacent to the unknown spectrogram. The known element should be one which has a large number of lines and for which suitable maps of the spectrogram of the element are available. For this purpose one usually uses the iron spectrogram which has been very carefully studied and mapped (Fig. 10). Quite a number of iron charts or guides have been prepared and published for the spectrographer; and some of these, in addition to having the wave length of the iron lines identified, have graduated scales and indicated positions of the persistent

and stronger lines of other elements marked adjacent to the iron spectrogram (Fig. 11). The process of identifying the presence of an element then becomes the simple comparison of adjacent spectra and checking in the tables as to the identity of the element. There are also available a number of charts of the spectrograms of individual elements which permit a rapid identification by superposition of spectrograms; in the case of identity of a single line by means of the iron scale spectrogram, it is possible

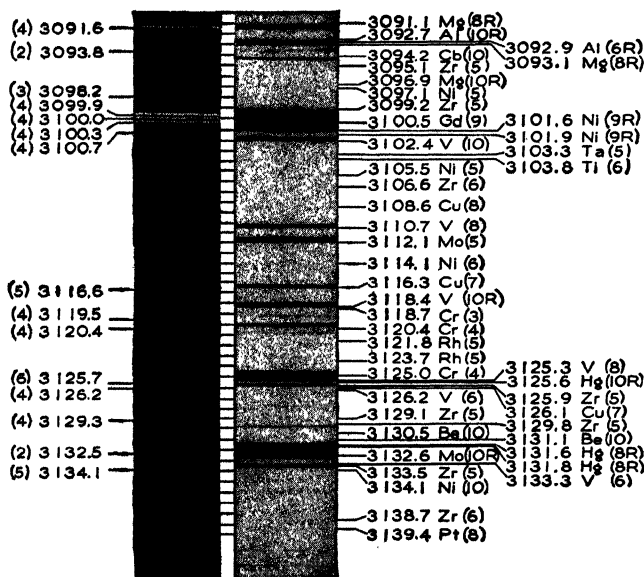


Fig. 12.—Use of cards for identification of elements. Projection of unknown spectrogram with enlargement to the same scale as the card spectrum. (Note: In this example the unknown is an iron-containing compound and hence no adjacent iron spectrum is required.)

to identify the other lines of that element by superposition or adjacent comparison of the spectrogram of the unknown element in the chart or negative form (Fig. 12). Many laboratories which are required to do a variety of qualitative examinations will have collections of spectrograms of pure elements or their salts which can be used to compare with unknown spectrograms to eliminate all lines of the unknown of the element in question and determine which lines are impurity lines requiring further measurement and identification.

3. Quantitative Analysis

It was suggested in the earliest work in qualitative spectroscopy that the amount of the element might be estimated from the intensity of the spectrum line, but for a long time this method did not appear to be practical except for a very rough semiquantitative estimate. Following the development of the theory of origin of spectra and the knowledge of the significance of certain line combinations, it was found possible to choose certain lines and combinations of lines which by accurate measurement were found to vary proportionally to the concentration of the element present. For trace analysis, the line intensity of even the strongest lines is such as to limit the use of visual methods. The photographic method has therefore been essential, since it is an integrating method which adds the weaker effects on long exposure to give a visible photographic effect.

The measurement of light intensity by means of blackening of the photographic image is not a simple linear function. Hence it will be essential to consider this measurement briefly before discussing the general methods of quantitative spectrographic analysis. In Figure 13 is shown the relation between observed density of the photographic image and the intensity

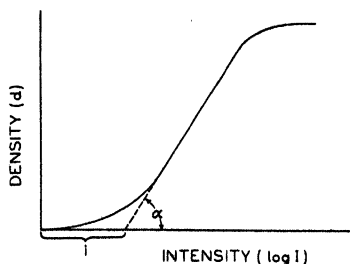


Fig. 13.—Density vs. log intensity for a photographic emulsion.

$\tan \alpha = \gamma$ (the gamma or contrast factor of the emulsion),
 i = inertia.

of light producing the effect, where other factors such as emulsion, time of exposure, temperature of developer, time of development and character of developer are kept constant. It will be noted that there is an initial portion representing a certain low intensity in which there is an inertia or lag of density with respect to light intensity, following which there is a region of nearly linear relationship between intensity and density. After this second linear region there is a third region in which the rate of density increase with intensity gradually drops to zero and a maximum of photographic density is reached. By careful study of photographic emulsions, it has been found that, with all variable factors controlled, except the wave length of the exciting light, a different slope of density-intensity curve will be obtained. This limits, of course, the spectral range over which comparisons in intensity of lines can be made, and has resulted in the production of special emulsions for photographic spectrophotometry, in which a nearly constant slope or *gamma* is obtained in different spectral regions (Fig. 14). The slope of the density-log intensity curve in the

linear portion can be expressed as the tangent of the angle formed by the interception of the extended linear portion with the abscissa. This value is commonly referred to as the gamma (γ) of the emulsion and is an indication of the contrast or density range of the emulsion.

In many spectrographic procedures it is more convenient to operate on a time rather than intensity basis; and, since the total number of lumens or units of light energy that strike the photographic emulsion are determined by the product of the light intensity and time of exposure, one can obtain a similar gamma value through a study of densities obtained from a source of constant intensity with varying lengths of exposure, rather than unit time values and varied intensities of the light source.

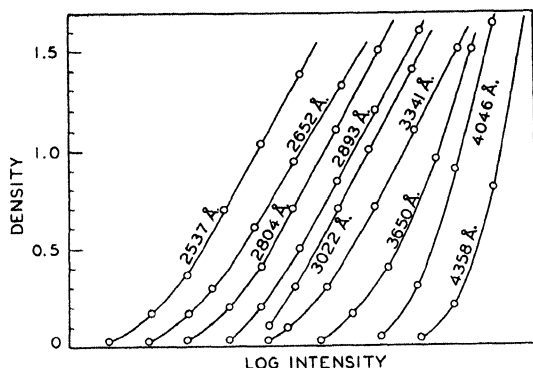


Fig. 14.—Variation of gamma with wave length for process plate.

In a similar analogy, the density of the line on the plate may be considered as a function of the density obtained by exposure of a constant intensity source for a given length of time, or as that intensity obtained by the ignition of a weighed amount of sample. The optical densities of lines obtained by either of these two methods may be compared with a series of standards containing known amounts of the element to be analyzed and exposed under similar conditions. This method of comparison of the unknown with a series of known standards removes to some extent the necessity of knowing the plate characteristics, since at equal densities the intensity will be equal and no reference to the emulsion gamma will be necessary.

The determination of the amount of element present by an absolute measurement of the total amount of energy produced from a given weight of sample or for a given exposure of uniform intensity requires in many

cases a careful control of the source with regard to voltage, amperage, focus and general alignment, so that serious errors are quite possible in the determination. As a means of removing some of these errors, a method has been devised which is known as the internal standard method. In this procedure, a known added amount of an internal standard is incorporated with the unknown or, in cases in which there is a known major constituent which is reasonably constant, one of the weaker lines of this major constituent may be chosen as the internal standard line. The intensity of the unknown line is determined not as an absolute value, but rather as a relative value as compared with the internal standard line. By this method, variations in exposure, arc intensity, focus and alignment will cause concomitant effects in both lines to be measured, but will not affect the ratio of intensities of the chosen pair of lines.

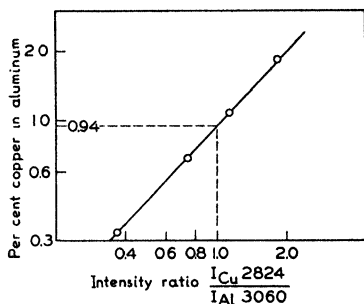


Fig. 15.—Working curve for the determination of the per cent copper in aluminum base alloy. The index point (0.94%) is indicated as the concentration of Cu which gives the Cu line and Al line of equal intensities.

As was indicated in the brief discussion on the origin of spectrum lines, the degree of ionization and other electrical influences will determine the intensity of certain lines in the spectrum. It will, therefore, be necessary to choose, as line pairs of unknown and internal standard elements, lines which represent the same degree of ionization and which respond in a similar manner to electrical or energy influences. Such pairs are known as homologous pairs. The fact that some lines do not respond in the same manner as others, because of differences in ionization potential, may be used as a means of controlling or defining the excitation conditions. These latter pairs are usually chosen from lines of the same element, representing different degrees of ionization, and are known as control pairs. For purposes of quantitative analysis, these homologous pairs have been chosen to avoid interference due to coincidence of lines of other possible elements, and to be within the same region of the spectrum so as to avoid excessive corrections due to changes in gamma of the emulsion. This will also permit observation of all lines at a single setting of the spectrograph if

the instrument is one of the Littrow type requiring several settings for a complete spectrogram.

A working curve for quantitative analysis represents the ratio of the intensity of the homologous pair of unknown and internal standard lines for the concentration range which is to be measured. The range to be measured can often be extended by the choice of several unknown lines of different intensity (Fig. 15). It has also been shown that the working curves are influenced by the presence of a third or extraneous element

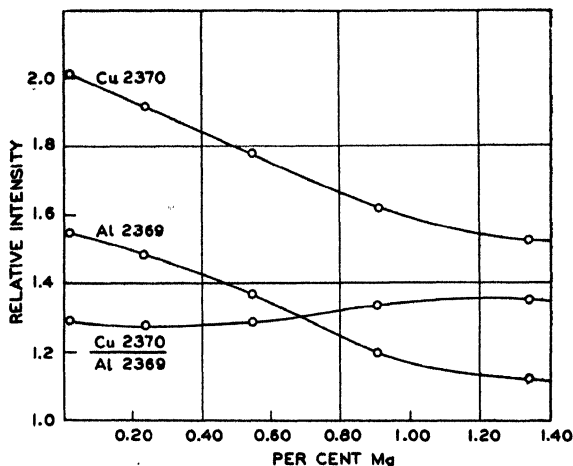


Fig. 16.—Influence of magnesium on the copper-aluminum intensity ratio.

which will alter the intensity of one element line without affecting the other (Fig. 16). Because of this extraneous element effect, it is often necessary to establish separate working curves for certain element combinations. The necessity of such special working curves limits the usefulness and accuracy of the spectrographic method to miscellaneous quantitative analysis; but where the analysis is of a routine type and a large number of similar samples are to be studied, as in the control of certain alloys, the preparation of working curves or factors can be easily accomplished and represents very little additional work as compared with the analysis of a large number of unknowns.

The advantages of quantitative spectrographic analysis are largely in the routine speed which can be attained and the relative accuracy of analysis for low concentration. There are a number of necessary steps in making the analysis; but where large numbers of samples of similar

composition are to be analyzed the time involved in certain control steps becomes negligible when distributed over the large number of samples. Quantitative spectrographic analysis is, therefore, not very satisfactory for individual analyses unless other methods are not available.

It will be helpful to follow through the various essential steps involved in present-day commercial analysis. From the illustration chosen it is hoped that some idea of the speed and accuracy attainable may be apparent. In order to determine properly the intensity of spectrum lines,

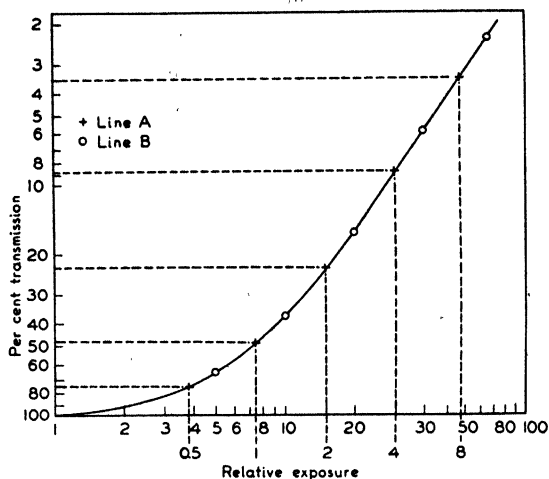


Fig. 17.—Film calibration curve using data from Table VI obtained with a five-step $2\times$ sector.

it will be necessary to calibrate the photographic emulsion in terms of its response to light intensity. In this calibration one may use a step sector in front of the slit so as to reduce the intensity of spectrum lines by known amounts. In the example in Figure 17, a step sector with openings corresponding to apertures of 2, 4, 8, 16 and 32 was used, each adjacent opening transmitting with a factor of $2\times$. It is possible to choose any one of these steps as that of unit light intensity, *i. e.*, step 2 = 1 (unit intensity); then the relative transmissions of the sector will be $1/2$, 1, 2, 4 and 8 times unit intensity. On a log-log scale or graph, the per cent of light transmitted by different steps on the film may be set on the vertical scale against the known relative intensity (Table VI, page 88).

These five values are all obtained from a single spectrum line (line A). If another line is used which is slightly weaker than line A, the observed per cent transmission might appear as line B in Table VI. Setting the

vertical sliding scale so that any of the observed transmission values (such as 13) are on the linear portion of the curve obtained from line A, then the horizontal sliding scale can be set at unity against the vertical index line and the remaining line B values are plotted on the graph by sliding the vertical scale to the corresponding value ($1/4$, $1/2$, 2, 4, etc.) on the horizontal scale. Repeating this process with several darker and lighter lines will yield a sufficient number of points to determine accu-

TABLE VI
FILM CALIBRATION DATA

Step No.	Relative exposure	Per cent transmission	
		Line A	Line B
1	0.5	75	65
2 ^a	1	48	37
3	2	23	16
4	4	8.8	6
5	8	3.5	2.1

Arbitrarily assigned relative exposure of unity.

rately the calibration curve. It should be noted that, by using a sufficient number of lines of different intensity, a fewer number of steps are essential in the step sector. In many commercial installations the calibration is done by the use of a simple two step sector. The steps need not be cut on a twofold ratio and can be any whole number or fractional ratio providing the ratio is known.

TABLE VII
RELATIVE INTENSITIES OF IRON LINES FOR PLATE CALIBRATION
(8-amp. d.-c. arc)^a

Wave length, Ångström	Relative intensity	Wave length, Ångström	Relative intensity	Wave length, Ångström	Relative intensity
3153.2	1.11	3175.4	1.38	3217.3	1.51
57.0	1.29	78.0	1.29	22.0	1.81
57.8	1.18	3200.4	1.64	25.7	1.85
60.6	1.34	05.3	1.59	39.4	1.71
61.9	1.15	15.9	1.62	44.1	1.69

^a Dieke and Crosswhite, *J. Optical Soc. Am.*, 33, 425 (1943).

More recently, a series of iron lines has been carefully selected which have a constant difference in intensity over a considerable range of excita-

tion conditions. By means of these known intensity ratios it is possible to calibrate the emulsion without the use of a step sector, since in a single iron spectrogram a number of lines of known intensity ratio are obtained. The application of the method merely requires that the vertical index line be set at unity on the horizontal or intensity scale and the unity iron line

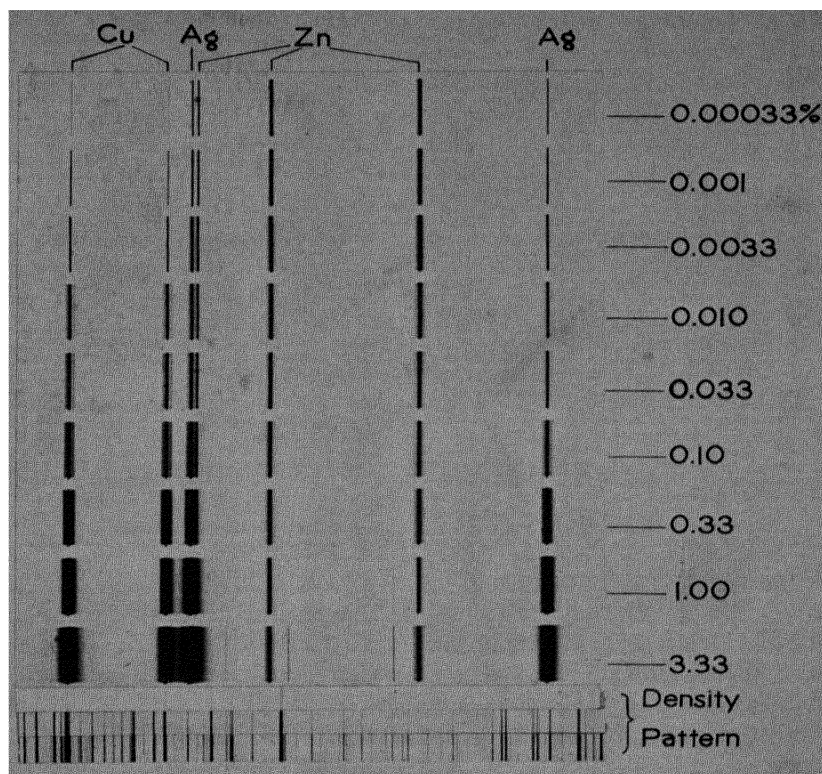


Fig. 18.—Spectrogram for preparation of densitometer working curve.

deflection plotted. The vertical scale is then moved to the other given iron line intensity ratio values and the corresponding deflections plotted so as to yield the necessary calibration curve. From this calibration curve it is possible to convert any observed transmission into the light intensity required for the photographic blackening of the emulsion, pro-

viding the emulsion, development conditions of time, temperature, concentration and other important factors are kept constant.

The next step in quantitative analysis is establishing a working curve, which is a graphical representation of the relative line intensity and concentration of the element producing the measured line (Fig. 18). Samples containing known amounts of standard and "unknown" elements are exposed under standard arc or spark conditions and the optical transmission for the selected homologous pair of lines is determined.

The transmission values are now converted into intensity ratios of the homologous pairs (Fig. 19) and these are plotted against the known per cent concentration of the "unknown" so as to produce the working curve (Fig. 15). Theoretically, this working curve, when plotted on a per cent

TABLE VIII
DATA FOR PREPARATION OF WORKING CURVE FOR COPPER IN ALUMINUM BASE^a

Copper concentration, %	Per cent transmission		Intensity ratio ^b I_{Cu}/I_{Al}
	Cu, 2824 Å	Al, 3060 Å	
0.33	83	48	0.37
0.64	64	51	0.78
1.09	44	49	1.25
1.90	25	47	2.20
1.82	26	45	1.90

^a See Figure 15.

^b Cu/Al index factor = 0.94.

versus I_0/I basis, should give a linear series of values with a zero origin. If the line crosses the zero per cent ordinate at a point above the zero ordinate value, then it should be extended until it does cross the zero transmission ordinate. The distance from the zero per cent point to the obtained intercept is thus an indication of the per cent of unknown element present as an impurity in the supposedly unknown free base material. A modification of this determination has been found useful in the quantitative estimation of trace elements in unknowns. The unknown is examined spectrographically, and we may suppose that a faint line of copper is noted at 3247 Å. To a known amount of this sample is then added a known small amount, say 5 mg., of copper and the spectrogram again observed. With a densitometer the densities of the copper lines in the two spectrograms can be determined, and their relative intensities determined with relation to an internal standard or principal component line. The ratio of the copper standard line intensities in the unknown sample is plotted

on the zero per cent or concentration ordinate and the ratio of the copper standard line intensities of the sample containing the 5 mg. added copper at the 5-mg. concentration ordinate. Connecting these two points by a line and extension of this line to the zero density value will give displacement on the base line or zero ordinate which, when compared proportionally to the 5-mg. spacing, will indicate the per cent or amount of copper present in the original unknown. The above method is often referred to as the

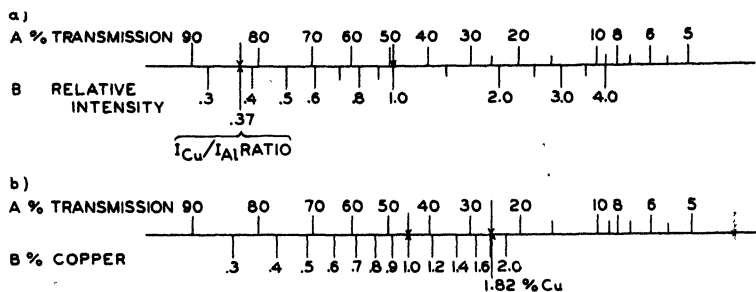


Fig. 19.—Example of slide rule settings for ratio of intensity and per cent concentration calculation.

(a) Scale A is formed from the intercepts of the transmission scale values with the calibration curve (Fig. 17), plotting their projected values on the intensity axis. Scale A might be termed a calibrated transmission scale. Scale B is the logarithm intensity scale. By setting unity on the intensity scale opposite the observed transmission value internal standard [Al line (48%)] the I_{Cu}/I_{Al} ratio of the observed Cu line transmission (85%) can be read directly from Scale B (0.37).

(b) Scale A is the same as above. Scale B is a concentration or analytical scale rather than an intensity scale and is obtained from Fig. 15. Over limited concentration ranges and in ideal cases of greater range the analytical scale is similar to the intensity scale multiplied by the appropriate index factor. In the example given in Table VIII the factor is 0.94. If this index value is set at the observed Al line transmission (45%), per cent Cu (1.82%) can be read directly from Scale B opposite the observed Cu line transmission (26%).

method of addition and is very useful in the analysis of individual unknowns where standard series for working curve preparation are not available.

The working curve data may be graphically recorded on a per cent or log per cent (or concentration) system. The projection of the working curve, when recorded on a log per cent basis, onto a scale produces an analytical scale in which the data are in per cent composition numerically, but spaced on a relative line density scale (Fig. 20). An index can be marked on the scale (0), at that point at which the concentration of the unknown element is such as to give a unit intensity ratio of standard and unknown line. One can also prepare a projected emulsion calibration scale in deflection values, and the two scales can be used as one would use a

slide rule. Since both scales are produced from logarithmic data, line intensity ratios can be directly determined and translated into per cent composition (Fig. 19b). The working curve, when plotted on a log per cent composition versus log intensity ratio basis, should give a linear series of values with a slope of 45° . Variations from 45° slope will be caused by self-absorption, reversal, and the influence of extraneous elements.

When large numbers of similar unknowns are to be handled, the use of the slide-rule method permits rapid calculation. The use of special analytical scales for different elements permits the scale to be so constructed as

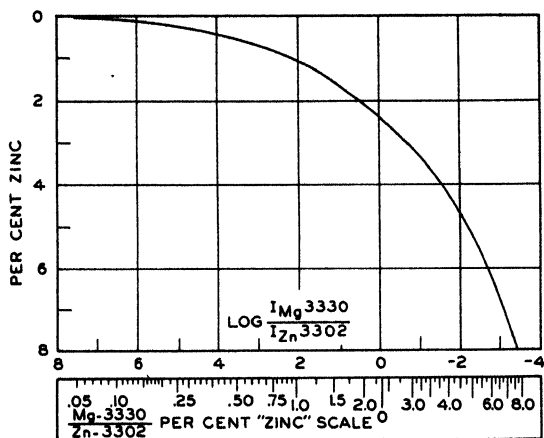


Fig. 20.—Preparation of analytical scale.

to take into consideration and correct for the above-mentioned reversal and extraneous element effects.

In the quantitative analysis of trace elements, the long exposures and high source intensity necessary to bring out the faint lines of the unknown produce a considerable amount of fogging of the emulsion, especially if there are lines of considerable intensity adjacent to the observed weak lines. This background is often necessary to bring up the line intensity to a measurable density, *i. e.*, if the true intensity were slightly less than the inertia intensity of the photographic emulsion, no line would be apparent. However, with a slight background, the resulting combination of the background intensity added to the line intensity may produce a total intensity which is greater than the inertia of the emulsion, and hence a measurable photographic image may be produced.

A method of correction for background has been suggested in which an

assumption is made that the background has a unit intensity. The intensity of the unknown line as observed on the spectrogram may be resolved into the true intensity of the unknown line plus the intensity of the background or the true line intensity plus one. In a sample analysis (Fig. 21), the observed background density amounted to 57% transmission (density of the spectrogram near the observed line). The transmission of the aluminum (internal standard) line was observed as 46%, and the transmission of the copper (unknown element) was observed as 32%. These observed aluminum and copper transmissions are actually the transmissions of the true line plus the background.

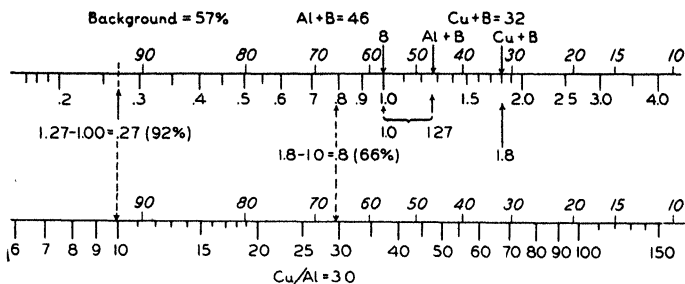


Fig. 21.—Example of slide-rule determination of background correction.

Setting 57% on the transmission scale of our slide rule, against 1 on the intensity scale (Fig. 21), the relative intensity of the aluminum line plus background is read opposite its transmission (46%) and is found to be 1.27; in a similar manner the intensity ratio of the copper line plus background is found to be 1.80. Subtracting 1 (background intensity) from these two values gives 0.27 and 0.80 as the relative intensities of these lines corrected for background. Reading back to the transmission scale, deflection values of 92% and 66% are obtained as the true deflections these two lines should have shown had there been no background. If, now, unity on the intensity scale is placed opposite the aluminum density (92%), the relative intensity of the copper with respect to the aluminum is found opposite the copper density value of 66% and is read as 3.0. From the working curve the per cent of copper can now be determined, or a projected analytical scale can be used in the last slide-rule calculation in place of the intensity scale. By setting the index (per cent of copper at which the Cu/Al line intensity is unity) opposite the aluminum line density, the per cent of copper is read directly opposite the observed deflection of the copper line.

By careful control of sample form, excitation conditions, emulsions, development, densitometry and calculation methods, it has been found possible to obtain routine analyses with an accuracy of from 1 to 3% of the amount of element present, *i. e.*, an aluminum sample containing 1.00% of copper would give on repeated analysis such values as 1.01, 1.03 and 0.98 for three determinations (Fig. 15).

TABLE IX
REPRODUCIBILITY TESTS. SUCCESSIVE ANALYSES OF THE SAME SAMPLE^a

Test	Si, %	Fe, %	Cu, %	Mn, %	Mg, %
1	0.43	0.44	3.98	0.67	0.60
2	0.43	0.41	3.82	0.66	0.61
3	0.43	0.42	3.89	0.67	0.61
4	0.44	0.46	4.05	0.68	0.61
5	0.43	0.44	4.00	0.66	0.60
6	0.44	0.42	4.05	0.63	0.60
7	0.44	0.40	4.08	0.63	0.62
8	0.42	0.40	4.14	0.63	0.62
9	0.41	0.40	3.89	0.63	0.59
10	0.42	0.40	4.08	0.65	0.60
Chemical analysis (2 locations)	0.41	0.43	4.11	0.65	0.63
	0.40	0.42	3.91	0.64	0.60

Average deviation of individual results from mean chemical result

5.9	4.7	2.4	2.8	1.6
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Average deviation from mean spectrographic result

1.7	4.1	2.2	2.8	1.3
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^a Churchill and Churchill, *J. Optical Soc. Am.*, **31**, 611 1941.

In many laboratories the spectrographic methods have almost completely replaced the gravimetric methods of quantitative analysis. Since the spectrographic methods are based on known samples developed through gravimetric methods of analysis or combination, there has developed a demand for known standard samples. These standard samples are particularly useful in control and metallurgical analyses where the unknowns are handled in metallic form and the standard alloys are in the same form. The *Aluminum Company of America* has prepared an extensive series of such standard samples to aid in control and identification of various aluminum alloys (Table X). Similar series of standards are also available for other types of alloys, such as those of magnesium and iron.

TABLE X
PARTIAL ANALYSIS DATA (IN PER CENT) ON A PORTION OF AVAILABLE ALCOA
SPECTROGRAPHIC STANDARDS^a

Sample No.	Si	Fe	Cu	Mn	Mg
SAC33	7.12	1.42	8.12	0.32	0.27
SAC48	2.83	1.40	4.92	0.22	0.08
SAC105	0.69	0.67	6.61	0.11	0.10
SAC107	3.06	0.37	4.93	0.04	0.04
SAC108	5.08	0.77	6.62	0.12	0.10
SAC110	0.21	0.27	4.96	0.04	0.03
SAC111	0.72	0.71	6.53	0.12	0.11
SAC112	1.59	1.50	8.03	0.33	0.30
SAC113	3.11	0.34	5.08	0.04	0.03
SAC114	5.12	0.77	6.50	0.11	0.10
SAC115	6.75	1.58	7.86	0.33	0.30

^a Brode and Scribner, *Report on Standards Samples for Spectrographic Analysis*. American Society for Testing Materials, Philadelphia, 1944.

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NOTE

Grateful acknowledgment is made to John Wiley and Sons, Inc., for permission to use several illustrations from their book, *Chemical Spectroscopy*, by Dr. Brode.

V. *Application of Absorption Spectra to Chemical Problems*

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THE PRECEDING CHAPTER discusses the application of spectroscopy to qualitative and quantitative methods of emission analysis for the elements. In this chapter, we shall apply to the absorption spectra of molecules some of the general principles which were previously discussed. And again we shall pass over the description of apparatus and methods of observation, although reference can be made to sources (1-5) where such equipment and methods are presented in considerable detail in the event of further interest in or need for this information. It will be essential, however, to consider briefly the methods of recording observed data, in order that we may be able to discuss with ease the significance and use of the data in the solution of chemical problems.

I. NOMENCLATURE

There is no very satisfactory agreement among research workers in the field of absorption spectrophotometry with regard to the methods of recording and describing their data. And while we do not claim that the methods described herein are the most ideal or satisfactory, we shall attempt to confine our discussions to a limited system of nomenclature, since, as we have already mentioned in connection with the subjects of

apparatus and methods, our primary object is to consider the application of spectrophotometric data to the solution of chemical problems.

As is diagrammatically indicated in Figure 5 (page 73, Chapter IV) the absorption of light is accompanied by the displacement of an electron to higher or outer levels in the atom; and since this absorption takes place in many atoms when in molecular combination, and in a liquid or solid physical state, rather than in a gaseous state, it is obvious that the amount of absorbed energy will be affected to some extent by the energy content of the molecule and the effect of surrounding atoms and molecules. This results in a broad or average band rather than a sharp line. These broad bands will have different intensities at different wave length values; hence it is necessary to record the intensity of absorption or optical density of the material as well as the wave length or frequency of the exciting light.

In the measurement of optical density, we may indicate the incident light intensity as I_0 and the transmitted light intensity as I . The transmission, T , may be indicated as the ratio of these intensities, I/I_0 , and the per cent of light transmitted thus becomes $100 \times T$. In accordance with Beer's and Lambert's laws, the following relationship between I and I_0 is found to hold:

$$I = I_0 \times 10^{-kcd}$$

where k is a constant for the wave length and compound under observation, c the concentration and d the depth or thickness of the cell. For solids of unknown concentration the c will drop out and the k will be assigned as a constant for the concentration as well as wave length and compound. The above equation can be converted to the following logarithmic expression:

$$kcd = -\log_{10} I/I_0$$

which is a more useful form, since the values k , c and d are the important factors in recording the observed data. Although the data which are plotted, $-\log_{10} I/I_0$, form a negative expression, it is usually recorded as a positive value in plotting so that the points of maximum absorption appear as peaks in the absorption curve.

Since k is a fixed constant, independent of concentration or thickness, c and d , and the observed value is the expression, $\log I/I_0$, or its equivalent which is kcd , it is obvious that this logarithmic expression is in itself a useful value record and may be indicated as $E = kcd$, where E is defined as the extinction coefficient or sometimes as merely extinction. The term k then becomes the specific extinction, *i. e.*, the extinction for a unit con-

centration and thickness. The same differentiation exists here between these extinction terms and terms used to record other physical properties, such as specific and observed rotation in polarimetry, and specific weight and mass. In polarimetric and other physical measurements, we also have values based on a molecular relation such as molecular rotation. A similar system is used in spectrophotometry with a unit known as molecular extinction, which is equivalent to the specific extinction, k , multiplied by the molecular weight of the compound under observation, and is usually designated by the symbol ϵ .

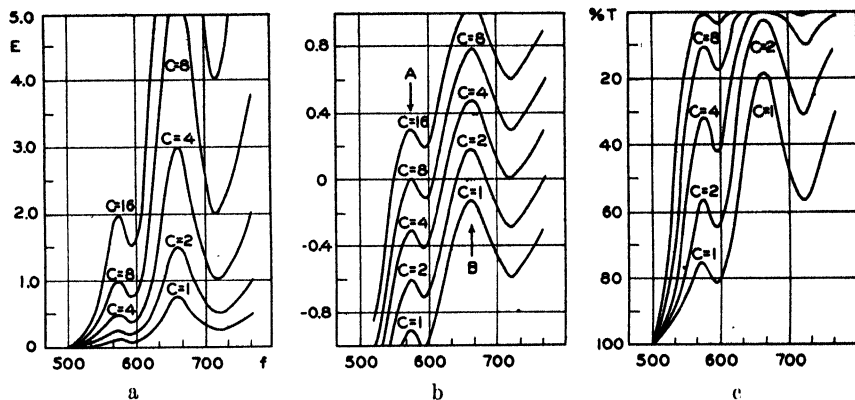


Fig. 1.—Graphic indication of absorption spectra.

a. Extinction (E) = $\log I_0/I$.

b. Log E .

c. Per cent transmission = $100 \times I/I_0$.

Because of the great differences in the extinction values of certain compounds, it is often more convenient to plot as ordinate values the $\log k$, $\log E$ or $\log \epsilon$, so as to permit a better comparison between compounds which show both weak and strong absorption values. It will be noticed in Figure 1 that the recording of $\log E$ values for the same compound at different concentrations will produce a curve of the same shape but of different ordinate values.

In the field of emission analysis, there is an almost universal acceptance of wave length as the system for recording data, and of the ångström unit (meters $\times 10^{-10}$), Å, as the unit of wave length. For reasons which will be indicated later, this same acceptance has not carried over into the field of absorption spectrophotometry. The accepted systems for recording absorption spectra data include wave length, wave number and frequency (described in the preceding chapter, page 70). Within the limits of the

visible spectrum, which are from 4000 to 7500 Å, it is a common practice to use millimicrons (meters $\times 10^{-9}$), $m\mu$, as the unit for abscissa values, since the accuracy of determination of absorption spectra data does not justify the additional significant figure indicated in the ångström unit. The visible spectrum is thus indicated as from 400 to 750 $m\mu$. In the infrared portion of the spectrum, the size of the wave length unit is increased to correspond with the increase in the numerical value so as to maintain a unit commensurate with the accuracy or significance of the

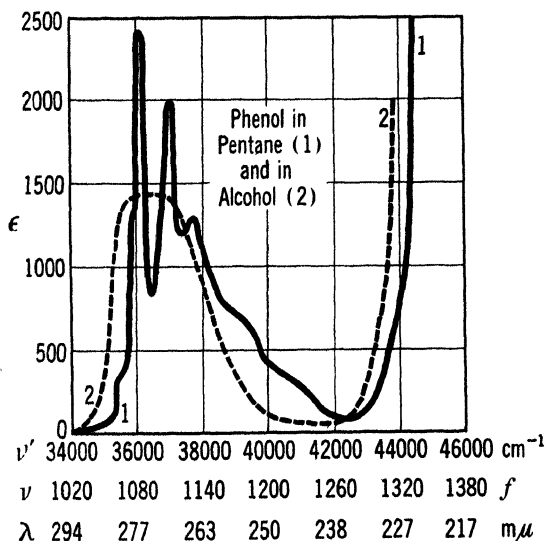


Fig. 2.—Absorption spectrum of phenol (note solvent effect).

data. In the infrared, the unit usually used is the micron (meters $\times 10^{-6}$), μ . For purposes of comparison it may be indicated that $1 \mu = 1000 m\mu = 10,000 \text{ Å}$.

The wave number, ν' , is the reciprocal of the wave length, λ , and is often used in recording absorption spectra data. A third system of recording abscissa values is in frequency, ν , which is approximately 3×10^{10} times the wave number. The data plotted in either frequency or wave number will appear exactly alike on the graph form, whereas, since the wave length data bear a reciprocal relation to the other two systems, the curve will be, in comparison, compacted toward the long wave length end and spread out toward the short wave length end of the graph. In

some compilations of data, all three of the abscissa data are given so as to satisfy all workers (Fig. 2). In general, the absorption spectra data are given in the wave length system in millimicron units ($m\mu$), in the wave number system in reciprocal centimeter units (cm.^{-1}) and in the frequency system in fresnel units (f) (vibrations per second $\times 10^{-12}$).

II. ABSORPTION AND RESONANCE

The absorption spectrum is a reversal of the effects which produce an emission spectrum in that atoms and molecules can absorb radiant energy of certain wave length or frequency values, with the resulting ejection of electrons from normal or ground states to higher levels. On return to their normal level, the electrons may emit energy in such forms as heat or light (fluorescence). The temperatures involved in the absorption phe-

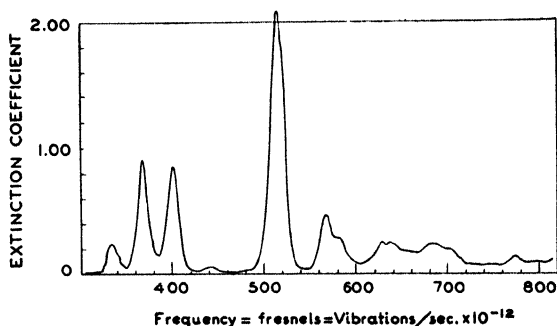


Fig. 3.—Tracing of extinction record of neodymium glass made on a recording spectrophotometer (6).

nomenon are such as to permit molecular as well as atomic combinations to take part in the effect, whereas in emission spectra most atomic combinations involved in molecular formations are broken apart by the heat or energy used in excitation, and only a few atomic combinations are sufficiently stable to produce molecular band spectra in the emission type of spectra.

The atoms which show absorption of light have, in general, an incomplete shell of electrons and, if this incomplete shell is buried within completed outer shells, there exists a partial insulation from external influences on this unsaturated shell. The resulting absorption of the atom with this protected shell is sharper and more regular, as is shown in the extremely sharp and almost linelike absorption bands of the rare earths (Fig. 3).

Other means of sharpening the bands and resolving broad bands into component structures include the lowering of the temperature so as to reduce

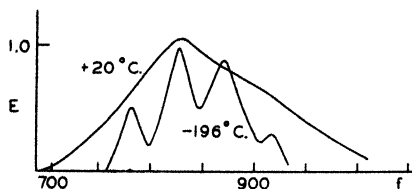


Fig. 4.—Influence of temperature on the resolution of component structure in absorption bands. Absorption spectrum of dodecapentanoic acid in ether-alcohol.

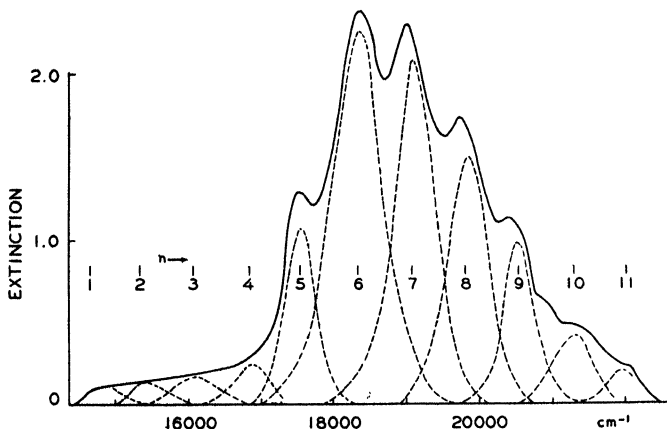
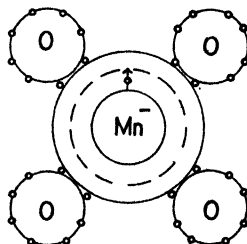


Fig. 5a.—Resolution of the absorption spectrum of an aqueous solution of potassium permanganate showing multiple frequency components.

Fig. 5b.—Schematic representation of electron shift in absorption in the permanganate ion (4). Note incomplete electron shell (broken line) with protecting outer shell (solid) formed with shared electrons from the oxygen atoms.



external influences (Fig. 4). Other means of protection of the unsaturated shell include increasing the number of outer electrons through the forma-

tion of molecules with symmetrically placed groupings so situated as to form a protecting layer (Fig. 5), by separating the molecules either in a vapor state (Fig. 6) or in a solution with a suitable insulating solvent (Fig. 2).



Fig. 6.—Absorption spectrum of benzene (vapor).

From the simple combinations of resonance that are possible in a single atom possessing an incomplete electron shell, we may pass to increasingly more complex molecular structures involving two positive nuclei which are deficient between each other with regard to completed electron shells. From the static point of view, we usually write such a combination, an example of which is the unsaturated carbon-carbon linkage, as a double bond. The compound ethylene is thus indicated as $\text{H}_2\text{C}=\text{CH}_2$ although it would be more correctly indicated in the light of our knowledge of electron sharing as $\text{H}_2\text{C}::\text{CH}_2$, in which each covalent bond is indicated by a shared pair of electrons. There are a number of possible electromers or electronic arrangements which can be written structurally for a double bond or two pair of shared electrons, and it is the summation of structures involved in shifting from one electromer to another which is termed resonance. In the limiting cases of these electromeric forms we would have the

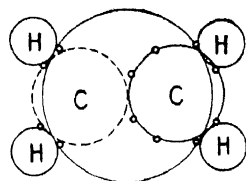


Fig. 7.—Quantitative representation of electron structure in one of the resonating states of ethylene. Note complete octet (outer circle) with complete and incomplete carbon shells within.

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TABLE I
IMPORTANT ORGANIC CHROMOPHORES

$\diagup \text{C}=\text{C} \diagdown$	Ethenylene	$\diagup \text{C}=\text{S}$	Thiocarbonyl
$\diagup \text{C}=\text{O}$	Carbonyl	$\diagup \text{C}=\text{N}-$	Azomethine
$-\text{N}=\text{N}-$	Azo	$\diagup \text{S}=\text{O}$	Sulfoxide
$-\text{N}=\text{O}$	Nitroso		

arrangement indicated in Figure 7, in which one carbon atom would be completely saturated or surrounded by a complete octet shell of electrons while the other carbon atom has but four electrons or an incomplete shell.

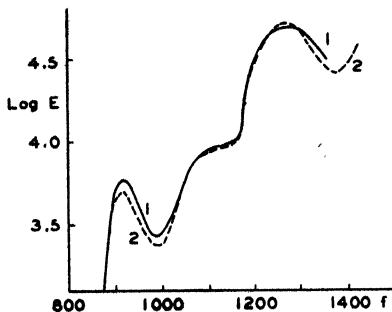


Fig. 8.—Insulating effect of methylene ($-\text{CH}_2-$) linkage between chromophores. Absorption spectra of: (1) veratrol + 1,3-dimethyl-6,7-methylene dioxyisoquinoline; (2) homoveratryl-3-methyl-6,7-methylene dioxyisoquinoline.

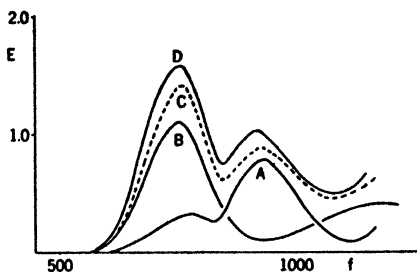


Fig. 9.—Separated chromophores. A and B are absorption spectra of two monoazo dyes, C the addition of these curves, and D the absorption spectrum of a disazo dye containing chromophores A and B coupled together by an insulating link.

The molecule as a whole may, however, be considered to have a complete octet outer shell. The passage of electrons from one shell to another,

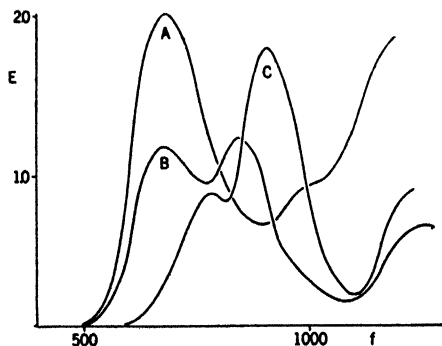


Fig. 10.—Conjugated and cumulative chromophores. Absorption spectra of disazo dyes, (A) with the two chromophores conjugated, (B) with the two chromophores cumulatively linked, and (C) with the two chromophores separated.

whether the shells or levels are part of the same or different nuclei in the same molecule, involves the absorption and emission of energy. The unsaturated ethenylene structure ($>\text{C}=\text{C}<$) is one of a number of un-

saturated combinations of atoms which are capable of resonance and absorption of radiant energy.

These simple resonating forms are known as chromophores and are essential for the pronounced absorption of radiant energy in organic compounds. The common organic chromophores are indicated in Table I. Molecules containing only one of these chromophoric groups do not as a rule show any absorption of visible radiant energy, but rather have ab-

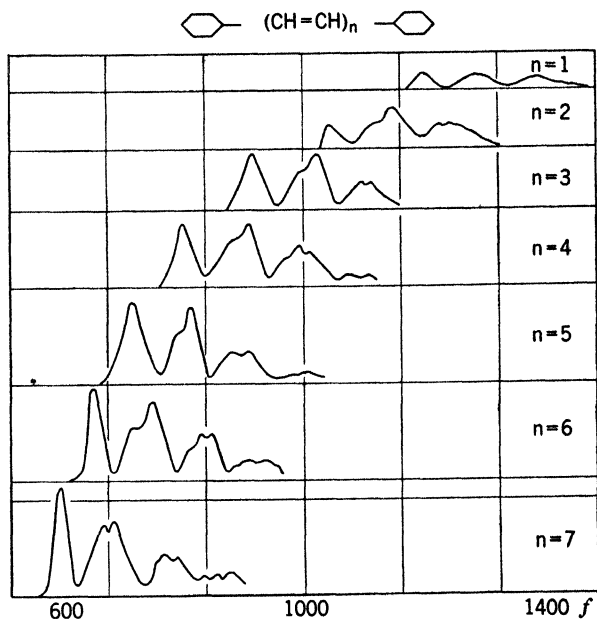


Fig. 11.—Effect of conjugation in polyethylene diphenyl derivatives, $\text{C}_6\text{H}_5-(\text{CH}=\text{CH})_n-\text{C}_6\text{H}_5$.

sorption in the extreme or low wave length portions of the ultraviolet. It is possible to combine chromophores together with resulting additive, multiplying or interfering effects. The shift of an absorption band may be toward longer or shorter wave length values and may involve an increase or a decrease in extinction. These effects may be defined as:

- (a) *Hyperchrome*: an increase in the extinction value of the absorption band. The intensity of the color increases.
- (b) *Hypochrome*: a decrease in the extinction value of the absorption band. The intensity of the color decreases.

(c) *Bathochrome*: a shift of the absorption band toward the red (lower frequency). The color deepens (*i. e.*, a change from yellow, to red, to purple, to blue, to green).

(d) *Hypsochrome*: a shift of the absorption band toward the blue (higher frequency). The color lightens (*i. e.*, a change from green, to blue, to purple, to red, to yellow).

The combination of two chromophoric groups may be (a) separated or insulated, (b) conjugated or (c) cumulated. Separated or insulated chromophores are those which, while in the same molecule, are coupled together by non-resonance-transmitting linkages so that the chromophores do not affect each other, and the absorption spectra observed is essentially that which would be produced by a solution of two separate compounds each containing one of the separated chromophores as its absorbing group (Figs. 8 and 9).

When two chromophores are separated by a single bond (a shared pair of electrons) the chromophores are said to be conjugated together, and a single chromophore is produced with a resulting bathochromic and hyperchromic effect (shift of the band toward the red end of the spectrum with an increasing intensity) on the absorption band as compared with the separate absorption spectra of the component chromophores (Figs. 10, 11 and 12).

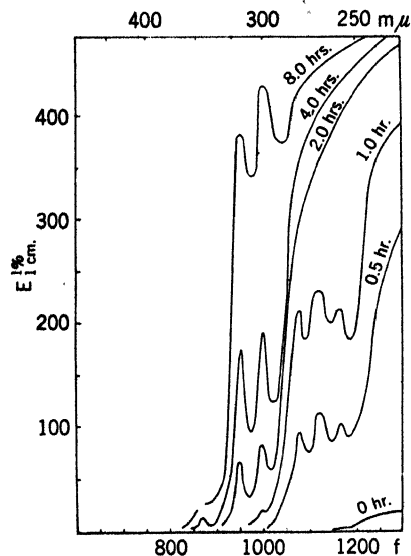


Fig. 12.—Absorption spectra of an isomerized unsaturated acid: curves indicate the change in the absorption spectra of the unsaturated acid heated with alkali for the indicated time.

The combination of two chromophores so as to share a portion of the resonating structure in common, such as the ketene structure ($\text{CH}_2=\text{C}=\text{O}$), is called cumulation and results in some interference. In the ketene example, the ethenylene structure ($>\text{C}=\text{C}<$) and the carbonyl structure ($>\text{C}=\text{O}$) are both attempting to resonate; at the same time there is some evidence of a complex chromophore involving both unsaturated portions as a unit (Fig. 10).

The usefulness of absorption spectra methods in the determination of

structure and concentration of organic matter depends on the existence of the chromophore units and their combination together to produce larger chromophores. There are many organic and inorganic compounds which do not show any selective absorption within the spectral regions which can be studied visually or with the aid of the photographic emulsion. (The discussion in this chapter has been confined to the visual and ultraviolet spectral regions since other radiant energy regions such as infrared, x-ray, etc., are discussed in other chapters in this series.) Such structures as water and the alkali and alkaline-earth hydroxides, halides, sulfates or carbonates, and many compounds such as the simple hydrocarbons,

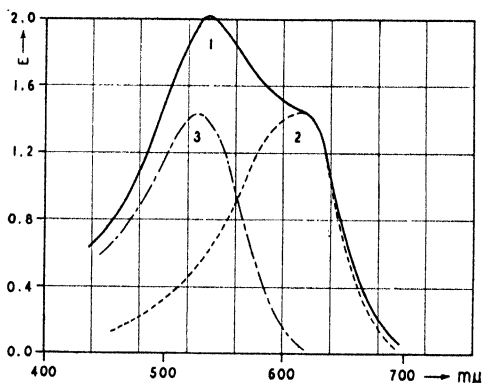


Fig. 13.—Absorption spectra (7) of: (1) Mother liquor from a 16% dyeing of a commercial sample of Agalma Black 10B whose shade was rated RRR by dyeing tests; (2) Agalma Black 10B spectrum; (3) impurity spectrum.

alcohols, carbohydrates and ethers, show no selective absorption. The absence of selective absorption by these compounds permits the study of solutions containing them and certain absorbing compounds, without the necessity of removal or extraction of the absorbing substance for examination. If the unknown mixture contains two or more absorbing compounds, even their identity and relative amounts can be determined if the absorption bands are sufficiently different in wave length or well enough defined to permit an estimation of their relative intensities (Fig. 13).

The simple absorbing groups, such as the ethenylene and carbonyl structures, produce selective absorption in the low wave length regions of the ultraviolet, but an increase in the number of these chromophores conjugated together results in a shift of the absorption band toward the visible and a deepening of the color until a multiple combination of the

ethenylene or other chromophores in a conjugated structure may result in colored compounds such as the yellow hydrocarbon pigment found in carrots and known as carotene (Figs. 14 and 15).

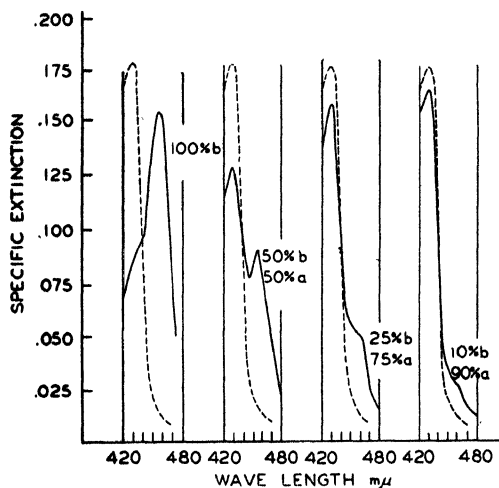


Fig. 14.—Absorption spectra of mixtures of chlorophylls *a* and *b* (solid line) and chlorophyll *a* (broken line).

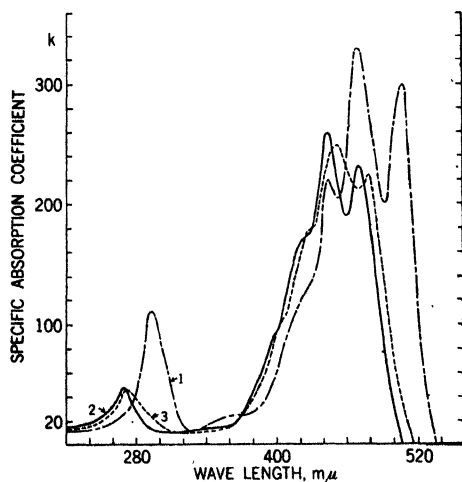


Fig. 15.—The absorption spectra (8) of: (1) lycopene, (2) alpha-carotene and (3) beta-carotene.

In general it may be said that the increase in mass of a compound results in a decrease in the frequency of vibration, although the effect is dependent in part on the position in the resonator to which the mass is attached. If the attachment to the chromophoric group is through an insulating atom or group, there will be little if any effect. If directly attached, it may be attached in such a position as to affect the frequency only slightly, or it may cause a complete breakdown of the normal frequency, such as is produced in a vibrating string when held or touched at a point between the two fixed ends. By attachment along the vibrating portion, or especially at the end, it may cause an increased amplitude of vibration as well as

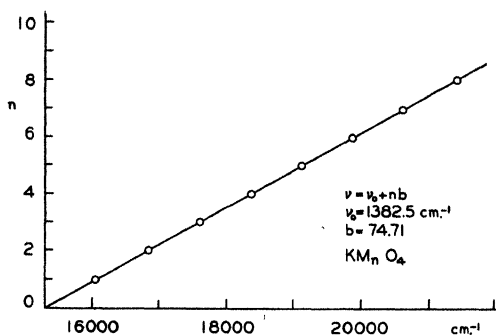


Fig. 16.—Relation between band multiple and frequency in the component band structures of potassium permanganate (see Fig. 5).

shift to a lower frequency. The comparatively simple compound, benzene, shows a complex spectrum which is resolvable into a series of uniformly spaced bands at multiple intervals of frequency corresponding to a fundamental absorption frequency in the infrared. These components are, in themselves, resolvable, as seen in the vapor spectrum of benzene; but, on the other hand, the observation of the absorption spectrum of benzene in a solvent shows a dampening of the vibration values so that broad bands rather than line structures are observed.

The use of a polar solvent or the introduction into the molecule of additional weighting groups results in further dampening. Eventually all indication of resolvable fine structure may be eliminated with the production of broad smooth bands, which, however, may represent multiple frequency values of a fundamental frequency.

The consistent appearance of multiple frequency effect in the several maxima exhibited by many compounds is an important argument for the recording of absorption spectra data on a frequency basis (Figs. 5 and 16).

In the classification of these various band systems it appears that one may have broad bands at widely spaced frequency intervals, which may be termed *principal* bands. These are few in number (from one to six in the spectral range from 200 to 700 $m\mu$), and are generally whole number or simple fraction multiples of a fundamental frequency. The lower members of this harmonic series are usually missing (Fig. 17).

The first apparent member of this series of principal bands is usually quite prominent, and, on increasing the number of conjugated groups in the chromophore, increasing the mass of the chromophoric portion of the

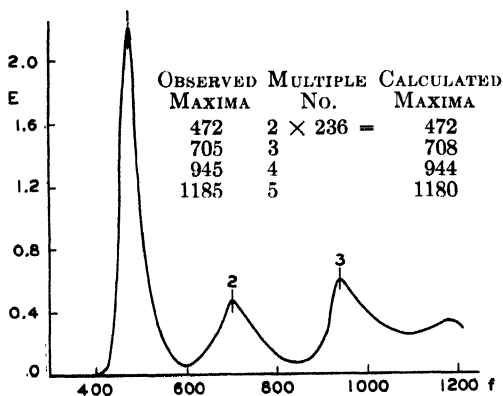


Fig. 17.—Absorption spectrum of Light Green SF Yellowish (Colour Index No. 670). Fundamental frequency = 236 f.

molecule or increasing the symmetry of the molecule, there is usually an enhancement of the first apparent member of this series as compared with the other members of the series (Fig. 18).

The *component* bands are those which make up the principal bands. These bands do not usually appear in solution spectra as separate or resolved components, but evidence themselves as inflections in the curve and in the form of an irregularly rather than a symmetrically shaped absorption band. As in the case of the principal bands, the component bands appear as multiples of a fundamental frequency, although a much smaller frequency value (*e. g.*, 5 to 20 f). These component bands also show a tendency for reduction of frequency and concentration of intensity of absorption in the first members of the series when the mass or conjugated character of the chromophore is increased. As is shown in the vapor spectrum of benzene, the component bands, when freed of the dampening

effects of solvents, may be resolved into *fine structure* (Fig. 6). The existence of multiple relations in these fine-structure bands are not clearly indicated.

The three types of absorption spectra bands which have been described above may be compared with the simpler band spectra which have been

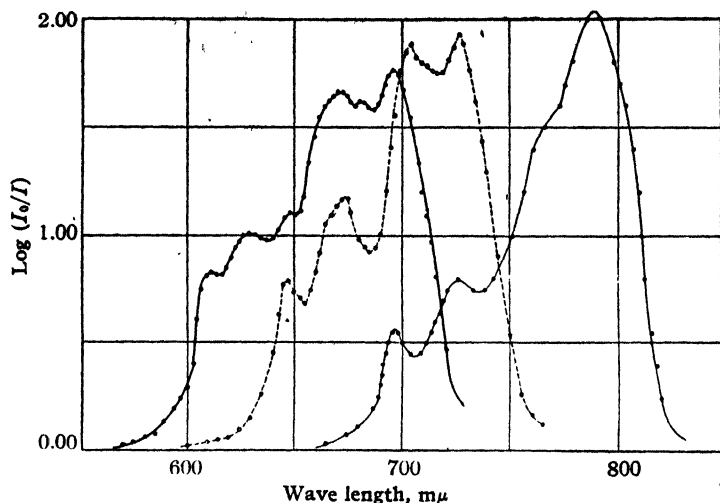


Fig. 18.—Absorption spectrum (9) of cobalt halides in their corresponding halogen acids: heavy solid line, CoCl_2 ; broken line, CoBr_2 ; light solid line, CoI_2 .

classified as electronic, rotational and vibrational effects. As has been pointed out in this discussion, however, there appears to be a transition from the simple types of monatomic and diatomic spectra, involving non-harmonic series of progression, to the apparent harmonic resonance of the large and complex organic and inorganic chromophores which appear to vibrate as a single absorbing unit.

1. Dampening Effects

In our discussion up to this point we have indicated the necessity of considering the dampening effects, the number and position of chromophores and the mass of the chromophoric groups in correlating structure to absorption spectra. We might, therefore, summarize the observed effects and indicate their application to the prediction of structure of the absorbing molecule.

Dampening effects are evidenced by the broadening of the absorption band and the loss of component appearance of the bands.

A. SOLUTION EFFECTS

The close proximity of other molecules prevents the unhindered oscillation of the chromophore. Polar solvents usually produce greater dampening effects than non-polar solvents in the presence of a non-polar chromophore nucleus (Fig. 2). On the other hand, ionic and strongly polar solvents (*e. g.*, CoCl_4^{--} in concentrated HCl) (Fig. 18) often show resolvable structure, which may be explained by the surrounding of the chromophore nucleus (CoCl_4^{--}) with ions (chloride) similar to its outer shell of atoms so that one could consider the effect of the solvent on the resonating atoms to be essentially the same as the effect of one chromophore on another.

In the application of these effects one might predict the polar nature of the chromophore from the change in band shape resulting from a change from polar to non-polar solvents.

B. MOLECULAR EFFECTS

Dampening of the chromophore may take place within the molecule, through the attachment of weighting groups or other chromophores at certain positions in the molecule. This effect may be of a dampening or resolving nature, since the added group may make the molecule symmetrical or unsymmetrical with regard to its chromophore structure.

Attachment of substituents in a non-symmetrical position may result in a broadening or dampening of the absorption band due to an increase in the number of chromophoric forms. Symmetrical attachment may cause only a greater amplitude without a change in shape, although there may be additional effects and even a complete

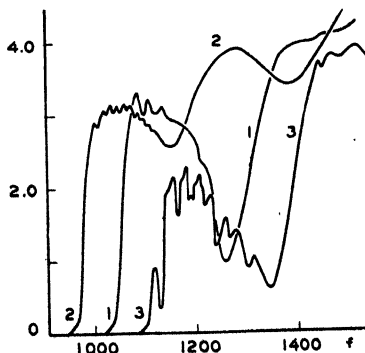


Fig. 19.—Absorption spectra of benzene and substituted derivatives: 1, phenol; 2, aniline; 3, benzene.

alteration of the chromophore as a result of attachment of additional weighting or absorbing groups (Fig. 19).

If the molecule consists of an outer shell of atoms surrounding the

chromophore nucleus, there will be a diminution of the dampening effect of the solvent in proportion to the thoroughness of this protecting shell. Such linkages as —O— , $\text{—CH}_2\text{—}$ and $\text{—CH}_2\text{—CH}_2\text{—}$ act as insulation connectors and prevent the transmission of chromophoric effects from one part of the molecule to another. If they completely surround the chromophore, they will act as a protecting shell. Weighting groups, which are not chromophores in themselves, will cause very little if any change in the chromophore if insulating connectors intervene between the weighting group and the chromophore.

2. Number and Arrangement of Chromophores

A. SEPARATED CHROMOPHORES

If the chromophores are in different molecules or are insulated from each other, the effect is generally that of addition of the two absorption curves of the separated chromophores (Fig. 9).

B. CONJUGATED CHROMOPHORES

If the chromophores are directly attached to each other by a covalent linkage (single bond), the two chromophores will combine to form a single larger chromophore. The effect of the chromophores on each other may be to counteract or repress vibration, although usually the effect is to enhance (Fig. 10). The enhanced effect is usually both hyperchromic and bathochromic in character (increase in absorption intensity and shift of the band center toward higher frequency).

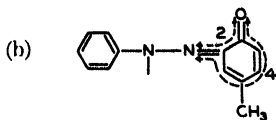
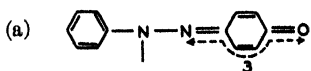
The combination of a number of chromophores through a conjugated (vibration-transmitting) linkage results in further bathochromic and hyperchromic effects, although there is a limit to the magnitude of these increases (Fig. 11). The larger chromophoric nuclei, unless protected sufficiently by a non-resonating layer, will become increasingly unstable as one increases the size of the chromophore. This introduces an additional limit to the effects which can be produced in the form of super-chromophores.

The chemical activity of a chromophoric system is markedly enhanced by an increase in the number of conjugated chromophores, and the terminal portion of the chromophore usually becomes the active or vulnerable point of the molecule. There are certain chromophores, such as the benzene ring, which are unusually stable (presumably because of an endless cycle of conjugated linkages in the ring structure), and appear to have no end position. The presence of these rings at the ends of a conjugated chain

promotes stability in the molecule. Another terminal group which acts as a stabilizer is the carboxyl ($-\text{COOH}$) radical.

In addition to stabilizing groups, there are groups which promote or enhance absorption. The latter are known as auxochromic groups and are sometimes classed as positive and negative auxochromes. These groups are usually attached to the benzene or stabilizing nuclei in an absorbing structure. (Note that the majority of the colored organic compounds contain stabilizing ring structures such as benzene.) The positive auxochromes include such groups as $\text{CH}_3\text{O}-$, $\text{HO}-$, NH_2- , $\text{CH}_3\text{NH}-$, $(\text{CH}_3)_2\text{N}-$, etc. The negative auxochromes include such groups as $-\text{NO}$, $-\text{NO}_2$, $=\text{CO}$, $-\text{CN}$, $-\text{N}=\text{N}-$, etc. Amphoteric auxochromes include such groups as $\text{>C}=\text{C}<$, $\text{>C}\cdot$, etc. A positive auxochrome produces an enhanced color in an acid solution, a negative auxochrome in a basic solution, and amphoteric auxochromes in either kind of solution. Since the effect of an auxochrome is to promote certain absorption effects and to act as a terminal group in the enhanced absorbing system, the auxochrome must be conjugated with the chromophoric group.

The number of conjugated linkages in a chromophoric structure has been shown to determine the position of the absorption band. An increase in the number of these linkages results in a proportional shift of the absorption bands to longer wave length values. The structure of phenylazophenol in its quinoid form (a) has a conjugated path involving three double bonds, whereas the 2-phenylazo-*p*-cresol (b) may be considered to have two possible chromophoric paths with either two double bonds or four double bonds. Comparing the absorption spectra of these two dyes, the first (a) shows a single principal band in alcohol at 855 f (Fig. 20) with a second band at 1280 f. The two bands are related in frequency since they bear the ratio of two and three times a



fundamental frequency of 427 f. On the other hand, the *ortho*-coupled dye (b) with two alternative conjugated paths shows a component absorption band in alcohol (Fig. 21) with frequencies at 770 f and 900 f in the principal band components. These *ortho*-coupled values do not appear to bear a simple relation as shown by the *para*-coupled values, but if one takes the average of the frequencies of the component parts of the principal *ortho*-coupled bands and compares it with the frequencies of the *para*-coupled bands, it will be noted that a similar relationship is present, as was shown in the simpler *para*-coupled dye. These component band

structures are also apparent in the absorption spectra observed in hydrochloric acid as a solvent.

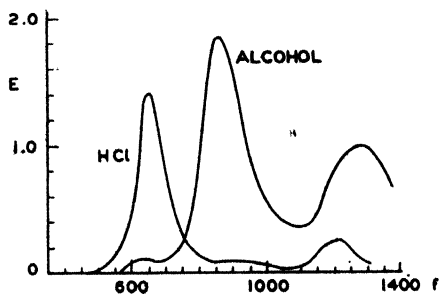


Fig. 20.—Absorption spectrum of *p*-phenylazophenol in alcohol and hydrochloric acid.

Neutral (alcohol)				Acid (HCl) (conc.)			
Band	Obs.	Calc.	(Harmonic)	Band	Obs.	Calc.	(Harmonic)
1	855	427 f	(1)	1	644	322 f	(1)
2	1280	854	(2)	2	922	644	(2)
		1281	(3)	3	1207	966	(3)
						1288	(4)

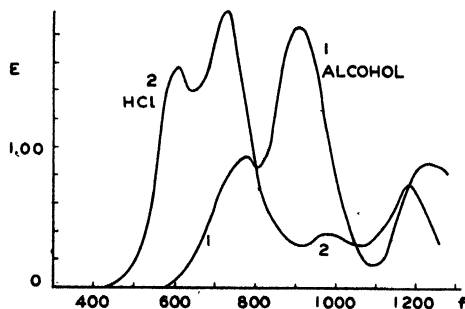


Fig. 21.—Absorption spectra of 2-phenylazo-*p*-cresol in alcohol and hydrochloric acid solution.

Neutral (alcohol)						Acid (HCl) (conc.)				
Band	Obs.	Av.	Diff.	Calc.	(H)	Band	Obs.	Av.	Diff.	(H)
1a	770	417	(1)	1a	600	331 (1)
1b	900	835	65	834	(2)	1b	725	662	62	662 (2)
	(1252)	(3)	2	980	993 (3)
						3a	1190	1324 (4)
						3b	(1458)	(1324)	134	1324 (4)
							

The close relationship between structural variation of chromophores and their absorption spectra is further demonstrated in the important applications which have been made in the use of absorption spectra to determine the structure of unknown compounds. This application has been of particular use in the study of medicinal and natural products available in very small quantities or those compounds which are highly unstable and difficult to remove or extract without decomposition.

Non-chromophoric substituents attached to chromophores have been shown to influence the character of the observed absorption spectra. There are a number of atoms and radicals which do not act as terminal groups or auxochromes. These groups can, however, be introduced into a chromophore system at various positions in the compound and produce what might be termed weighting effects. These weighting effects are, in a sense, similar to the effect of weight application to a vibrating wire in which the position of the weight attachment will influence the total vibration and the overtone characteristics of the resonating system.

Increased mass at a definite point (especially at a non-conjugated position) produces, in general, a decrease in the frequency of vibration, just as an increase in the mass of a vibrating wire will result in a decrease in the frequency of vibration (providing the tension is kept constant). In the same example of a vibrating string or wire, a change of tension will result in a change of frequency. In a like manner there are substituent groups in the vibrating molecule, including both auxochromic and non-auxochromic types, which produce effects equivalent to a tension change. It is difficult to separate or differentiate between tension and weighting effects, especially where the observed physical effect is the same. The differences in chlorine, bromine and iodine substituent effects in a chromophore are not alone the effects of increased mass, but include some tension effects due to a differing electronic structure. The tension weighting effects in this change of halogen include, in addition to a simple change of frequency due to increased mass, a change in the relative intensities of the component bands with a shift of intensity to the first principal and component bands (Fig. 18). Another excellent example of mass effects is shown in the metallic porphyrin derivatives in which changes of metallic coordinating elements from magnesium to tin, manganese and lead result in a general shift of the band to higher wave lengths and at the same time a shift of the center of vibrational intensity from the lower to the higher wave length components.

The tension weighting effects are difficult to distinguish. A mere change of position of substitution may result in a change in the frequency position

of the absorption band, such as might be predicted from a change in mass. An excellent example of this is found in the frequency shifts occurring in the sulfonic acid derivatives of phenylazo- α -naphthylamine and the corresponding β -naphthylamine derivatives (Fig. 22).

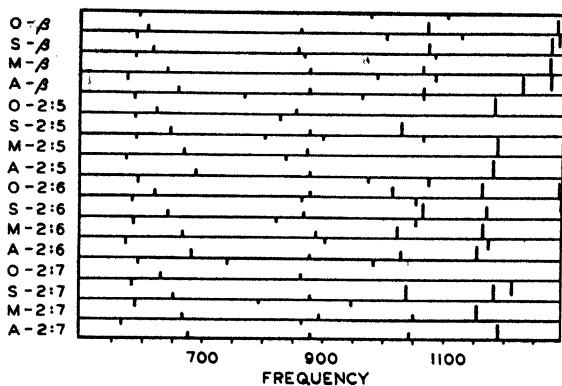


Fig. 22.—Frequencies of the principal maxima of mono-azo dyes derived from diazotized aniline, orthanilic, metanilic and sulfanilic acids coupled to β -naphthylamine and the indicated sulfonated naphthylamines (10). The lengths of the lines are relative measures of the intensities of the maxima they represent. Lines pointing upward represent neutral maxima; suspended lines represent acid maxima.

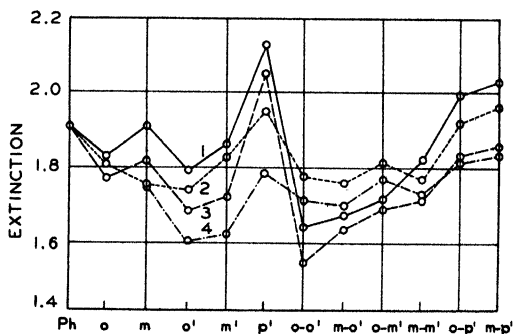


Fig. 23.—Influence of position of substitution in phenylazophenol on the extinction coefficient of the principal absorption band in alcohol solution. Curve 1, Br; 2, CH_3 ; 3, Cl; 4, NO_2 .

Series of position isomers whose absorption spectra have been studied are the methyl, chloro, bromo and nitro derivatives of phenylazophenol (Fig. 23). In this series it has been shown that the p' constituents (which

involved lengthening the molecule) result in enhanced absorption intensity; whereas *o'* and *m* substituents which are centrally placed in the chromophore result in depression of absorption intensity. While these effects are similar in a number of solvent studies, it should be pointed out that, in a sodium hydroxide solution, the principal bands are split into a two-component structure. The summation of the two-component intensities, however, conforms to the same variation in total intensity as is observed in the other solvents. In addition, there is an equilibrium between the component parts (Fig. 24) which is directly influenced by the position of the substituent.

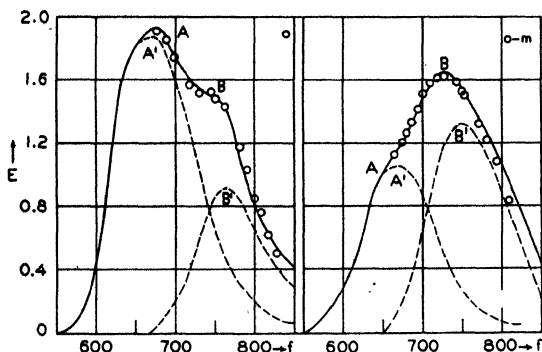


Fig. 24.—The analysis of observed absorption bands into component curves. These curves represent the absorption spectra of phenylazo-*o*-cresol (*o*), and *o*-tolylazo-*m*-cresol (*o-m*) in a 3% aqueous solution of sodium hydroxide. The circles on the graphs indicate values obtained from addition of the component bands A' and B'.

Brooker has shown, in an interesting series of simple and mixed chromophores which are conjugated together by ethenylene linkage to form a single complex resonating system, that there will be a deviation in the predicted position of the mixed chromophore band as compared with the observed position of the simple chromophoric structures and that the degree of divergence is dependent upon the relative polarity differences of the two chromophores. From these cases it would appear that the position and character of substituents may produce effects other than a mere shift of frequency, and a change in position may produce effects in a frequency shift which might have been predicted as resulting from a change of mass.

There are numerous practical examples in which the absorption spectra methods have been applied to study reaction rates, solution effects and tautomeric equilibria, in addition to the structural identification and

quantitative estimation which have been indicated above. Two examples may be cited: the determination of hydrogen-ion concentration; and the existence of intermediate compounds in solution form. In a study of the absorption spectra of indicators it has been shown that there is a definite relation between the extinction coefficient and hydrogen-ion concentration (Fig. 25) and that, when the extinction at the maxima of the absorption band is plotted against the hydrogen-ion concentration, the dissociation constant of the indicator can be directly observed from the

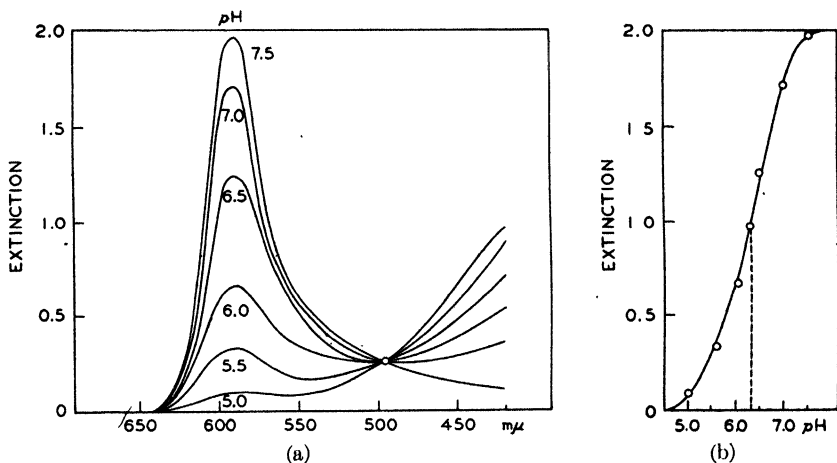


Fig. 25.—Spectrophotometric determination of hydrogen-ion concentration (11). (a) Absorption spectra of bromocresol purple at the indicated pH values; note isosbestic point at 498 mμ. (b) The dissociation curve calculated from the extinction and pH values. (Broken line indicates dissociation constant for the indicator.)

inflection point in the curve. Another interesting point which can be noted in Figure 25 is that the series of curves, representing the absorption spectra of the indicator at different hydrogen-ion concentrations, all intersect at a common point which is called the isosbestic point (point of equal extinction). From this isosbestic point it is possible to determine the concentration of the indicator regardless of the pH value of the solution; conversely, the hydrogen-ion concentration can be determined from the ratio of the extinction values at the band maximum and isosbestic point without the necessity of knowing the amount of indicator added.

The addition of hydrochloric acid to a quinoline solution of cobalt chloride will eventually convert the cobalt quinoline complex (CoQ_2X_2) to the cobalt halide complex (CoX_4). As shown in Figure 26, the absorption spectra changes have been studied at frequent dilution intervals.

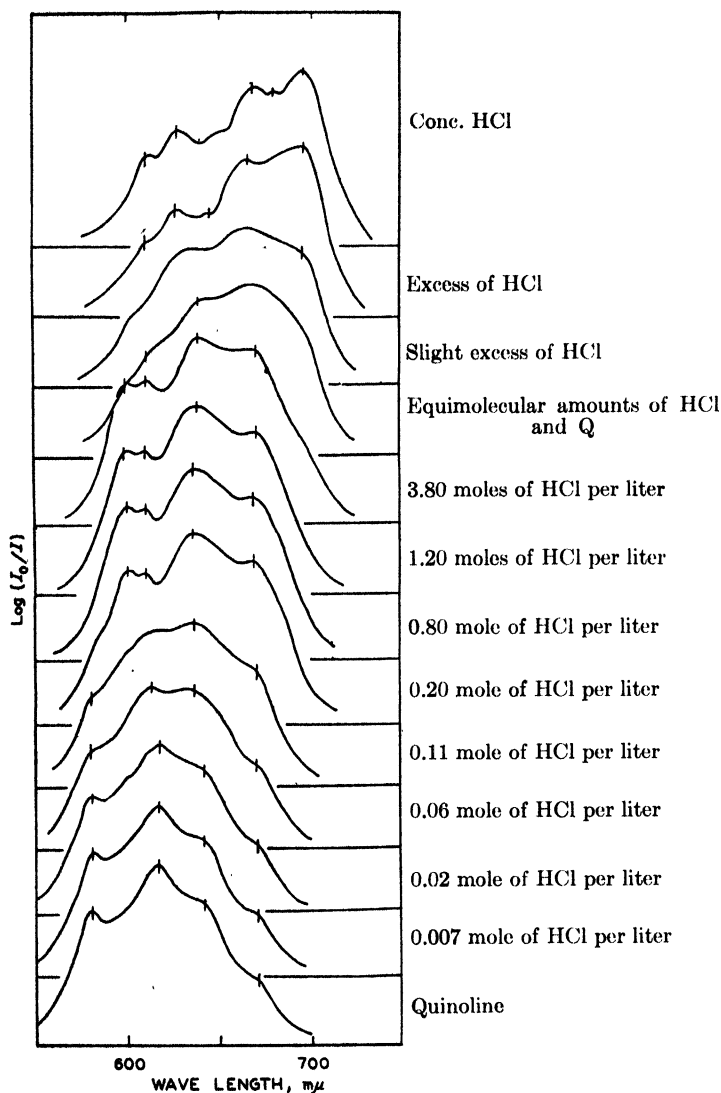


Fig. 26.—The changes from the “Py-Q” (pyridine-quinoline) system, through the “intermediate” system in the “HX” (halogen-acid) system, caused by the addition of hydrochloric acid to a solution of cobalt chloride in quinoline (9). These are only a few of the some fifty curves observed at various quinoline-hydrochloric acid concentrations, and have been chosen to show characteristic stages of transition points in the change of the absorption systems. The cobalt chloride concentration in all solutions was approximately 0.0043 mole per liter. Solvent concentrations are shown on the right.

The curves in this figure are only a few of some fifty curves observed at various quinoline-hydrochloric acid concentrations. It is to be noted that, at a concentration corresponding to a composition of (CoQX_3) , there appears a well-defined absorption spectra curve which is quite different from either of the end compounds and, therefore, indicates an intermediate structure.

The existence of mixed chloro-bromo cobalt complex salts in the presence of the pure chloro and bromo salts has been demonstrated by absorption spectra methods in which it was shown that the mixed chloro-bromo salt gave a spectrum with band frequencies intermediate between those of the pure chloro and bromo salts. The mixture of pure chloro and bromo salts gives an absorption spectrum similar to that which would be produced by addition of the absorption curves of the pure components, showing a marked difference in comparison with the absorption spectra of chloro-bromo complex salts.

By the application of the observations which have been discussed to the absorption spectra data of unknown compounds or series of compounds, it is possible to draw some rather definite conclusions with regard to the structure of the chromophoric substance. It is a rather generally accepted rule that similar (electronically similar) chromophores will produce similar absorption. The application of this principle has been most effective in the prediction of the structure of unknown substances. In cases in which there was some deviation in the spectra of two compounds, and especially where the deviation was that of position of the band with practically identical band shapes in both cases, it has been possible to apply certain of the principles discussed concerning the effect of substituent groups as a means of predicting the difference in structure of the two compounds.

Many substances, such as benzene, vitamin A, vitamin B₆, vitamin B₁, chlorophyll, etc., can be identified qualitatively and estimated quantitatively by their absorption spectra without the necessity of removal from their natural medium or solution by extraction or some other process. The absorption spectra of chromophore-containing compounds thus prove useful in the qualitative identification and quantitative estimation of compounds of known structure and properties, as well as in the prediction of the structure of unknown chromophores.

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VI. *The Infrared Spectrometer and Its Application*

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T

I. INTRODUCTION

THE NUMBER OF INFRARED SPECTROMETERS which are being used in the industrial laboratories of this country has recently increased manyfold. When one considers the unique possibilities of spectrochemical methods, and in particular those offered by infrared spectroscopy, the sudden increase in the popularity of this particular physical tool is by no means surprising. On the contrary, for a complete understanding of this fact one need only consider that, in connection with many vital industrial processes, a variety of analyses are being completed today by infrared methods in a matter of minutes. Many of these same analyses were previously not attempted at all, or at best were only performed with difficulty by more conventional methods.

This widespread acceptance of infrared spectrometers as an important part of the analytical equipment of industrial research and control laboratories is not attributable to the work of any one investigator, but rather to the diligent and persevering research of a number of distinguished scientists. Although many seemingly insurmountable experimental difficulties were encountered, these were overcome one by one, until now the performance of a modern infrared spectrometer far surpasses the fondest hopes of the research workers of earlier days.

At present, many different types of instruments are included among those

in use; they cover a wide range of dispersion, resolving power, sensitivity, accuracy and cost, and have been designed in most cases to meet the analytical requirements imposed by the specific problems for which they are used. The problems range from pure research on the structure of complicated organic molecules, through analyses of multicomponent mixtures of chemically similar compounds, to automatic production control. Before discussing these spectrometers and their applications, a brief description of the early days of infrared spectroscopy and of the origin of infrared spectra is in order.

II. HISTORY AND DEVELOPMENT OF INFRARED

Today we recognize the fact that x-rays, ultraviolet, visible and infrared radiation, and radio waves are similar in nature and compose parts of the total electromagnetic spectrum. At the end of the eighteenth century, however, only the radiations of the visible portion of the spectrum were known, and the concept of electromagnetic vibrations had not yet been evolved. Accordingly, a great amount of the research in spectroscopy which was conducted after the discovery of extravisible radiations was of necessity pointed toward the establishment of their fundamental nature and identity. In view of our present knowledge of the structure of molecules and atoms, of the laws governing black-body radiation, of electromagnetic theory, of geometric optics and of the entire subject of spectroscopy, it is often difficult for us to avoid losing sight of the exacting nature of the basic questions which faced the pioneer workers in the field of infrared and set the course of their researches. A detailed discussion of this early work would be out of place in this paper; accordingly, for an interesting account the reader is referred to Kayser's *Handbuch der Spektroskopie*, Chapter I (1900).

Disturbed and intrigued by the heating of the glass lenses of his telescopes, Sir Frederick William Herschel (1) the eminent English astronomer who is often referred to as the father of modern astronomy, demonstrated in the year 1800 the existence of radiation beyond the red end of the solar spectrum.* Immediately following this important discovery, heated controversies arose as to the exact nature of this newly found radiant energy. In the absence of suitable theoretical considerations, Herschel devised and conducted a series of experiments designed to establish more firmly the existence of these "heat rays," to determine the exact manner in which they

* One year later, J. W. Ritter, *Gilbert's Ann.*, 7, 527 (1801), discovered the ultraviolet region of the spectrum by its photochemical action upon silver chloride.

were reflected and refracted by common substances and to show the ability which many materials possessed for transmitting these rays (Fig. 1). From these researches, Herschel erroneously became convinced that he had discovered a new kind of radiation—one fundamentally different from visible light. Contemporary experimenters disagreed with most of his con-

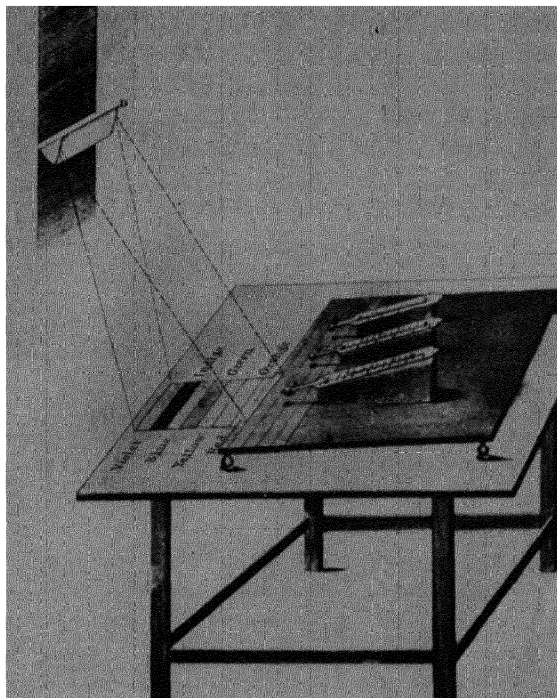


Fig. 1.—Herschel's drawing of the apparatus used in the discovery of infrared radiation.*

clusions and some even denied the existence of these rays. However, in 1840, his son, J. F. W. Herschel, convinced the Royal Society that he had not only succeeded in making the effect of the sun's infrared rays visible (Fig. 2), but that he had also proved they were not continuous, but consisted of several groups of rays. The regions in which he found practically

* This drawing appeared in a paper by Sir Frederick William Herschel in 1800 and is copied from the *Philosophical Transactions* of that year. The spectrum of sunlight produced by a prism was allowed to fall on a table. The temperature rise produced by radiation beyond the red was measured by one thermometer while the other two were used as controls.

no heat were recognized as the infrared analog of the Fraunhofer absorption lines (2).

Throughout the first hundred years of its history, many fundamental contributions to this branch of spectroscopy were made by such men as J. F. W. Herschel, Young, Wollaston, Fraunhofer, Brewster, Talbot, Kirchhoff, Fizeau, Foucault, Seebeck, Becquerel, Nobili, Melloni, Svanberg, Langley, Rubens, Boys, Angström, Aschkinass and Julius. Through their work the thermometers used by Herschel were replaced by sensitive thermocouples or bolometers, the crude arrangements of window shade slits and prisms first used by Newton and later by Herschel were replaced by spectrometers, black-body sources and salt prisms became available and a satisfactory beginning was made upon a thorough understanding of the in-

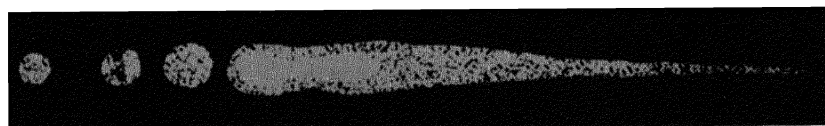


Fig. 2.—J. F. W. Herschel's picture of the sun's spectrum, produced by the differential evaporation of alcohol from a soot layer.

frared portion of the spectrum and of the interaction of these radiations with matter.

W. F. Julius (3) published in 1892 one of the most important papers of this era, for it was he who first showed the relation between infrared spectra and the structure of organic molecules. Having been impressed by the similarity of the spectra of chemically related molecules, he showed by empirical correlations that the presence of a methyl group always gave rise to a strong absorption at a wave length which appeared to be independent of the constitution of the rest of the molecule. Similar characteristic absorptions were discovered for hydroxyl groups, aromatic structures, amino and many other functional groups. Julius realized that the infrared spectrum of a molecule could be used for analytical purposes.

In 1905, the Carnegie Institute published the first of three volumes covering the infrared research which W. W. Coblentz (4) had conducted over a period of several years. In these volumes, Coblentz gave not only a complete discussion of instruments, methods and techniques, but also transmission and reflection data for a very wide range of organic and inorganic compounds. The findings of Julius were confirmed and greatly extended. So important was this monumental piece of work that it has served through-

out the intervening years as the foundation of every beginner's knowledge of infrared spectroscopy.

These classical papers and others of a similar nature firmly established the value and importance of infrared and excited the interest of many additional workers. At the same time they showed clearly that the maximum amount of information regarding the structure of the samples studied could be gained only if transmission curves could be obtained using spectrometers of considerably higher dispersion, resolving power and accuracy. Accordingly, while some investigators diligently applied the small spectrometers then available to a greater number and variety of problems, the undivided attention of many others once again turned to problems of instrumentation.

Infrared then entered a most fruitful quarter century, during which rapid strides were made along both theoretical and experimental lines. Such revolutionary innovations as the echelette grating for the near infrared, the wire grating for the far infrared, the use of off-axis parabolas as collimating mirrors, curved slits, vacuum thermocouples of special alloys and galvanometer amplifiers were introduced. Each such improvement led to infrared spectra of a higher quality, and furnished those interested in theory with more useful data upon which to build and with which to test their concepts of the origin and interpretation of absorption spectra. Figure 3 shows several curves of hydrogen chloride absorption as taken on a series of spectrometers of increasing resolution. Whereas a small prism spectrometer gave the crude transmission curve of a given sample quickly, the most elaborate and precise research spectrometers required many hours per compound. The detailed study of a large series of compounds thus became a most tedious task.

About 1935, the importance of infrared as a research tool for the study of organic structures and for the analysis of complex chemical mixtures again came to the fore. One or two industrial chemical laboratories instituted research programs on infrared. Immediately, automatic spectrometers became absolutely necessary, since to be of maximum value industrial analyses must be performed rapidly and accurately. This demand was met by adding to the large dispersion research spectrometers suitable electronic and mechanical features. Properly equipped, such an instrument can record in ten minutes as much infrared data as could formerly be obtained in some six to eight hours through the use of a manually operated spectrometer.* Already thousands of records have been taken on spectrometers of this

* None of the infrared instruments in use today is in the true sense an automatic recording spectrophotometer, and accordingly it is still necessary for the operator to calculate the transmission values from the data recorded.

type during the past few years, and the list of spectacular chemical analyses which have been completed is growing rapidly.

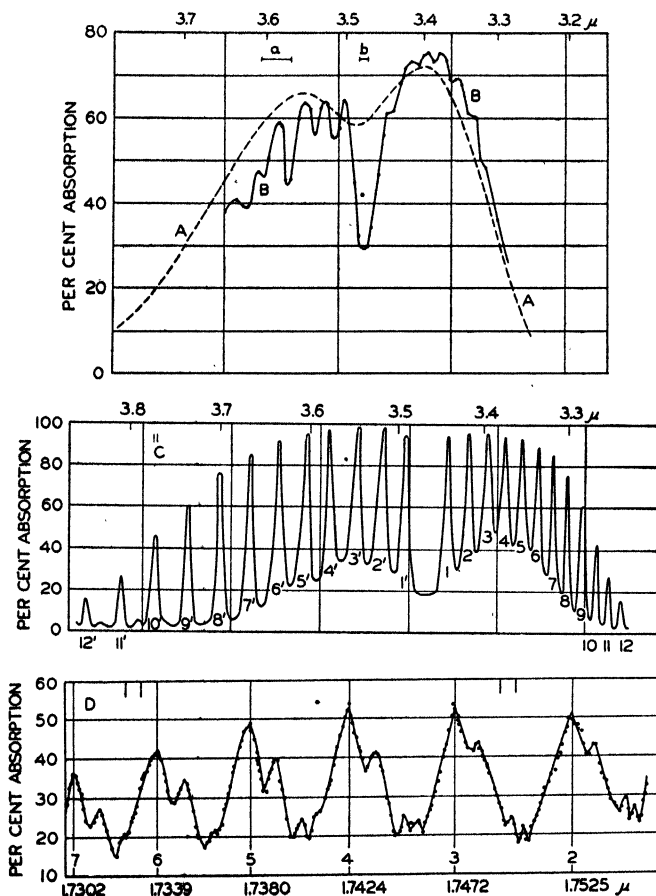


Fig. 3.—Successive steps in the investigation of the 3.46 μ HCl fundamental.

Curve A was obtained by Burmeister, in 1913, with a fluorite prism instrument; B by von Bahr, in 1913, with a quartz prism; and C by Imes, in 1919, with a grating spectrometer. Curve D shows a portion of the 1.76 μ overtone as obtained by Hettner and Böhme, in 1931.

It is interesting to note that the research-type spectrometers adopted by industrial laboratories employ large rock-salt prisms and not high-disper-

sion echelette gratings. In view of certain experimental difficulties attendant upon the use of gratings, it is fortunate that, at least for the present, the dispersion of a 16-cm. prism is sufficient for the average chemical analysis. Too much dispersion is, in fact, often a disadvantage.

The latest trend in infrared instrumentation is toward the use of small prism analytical-type spectrometers. Once the spectra of the individual constituents of a mixture have been recorded by a large spectrometer, it is very frequently possible to predict that the specific analysis in question could be performed by a simple spectrometer of low dispersion. For such purposes, at least two types of small instruments are being manufactured commercially. During the past two years more than fifty such instruments have been installed, and are already playing an important role in the present emergency.

The development of the subject of infrared spectroscopy from its discovery up to the present is outlined and summarized in the following three sections.

1. Instrumentation

Discovery of radiation beyond the red end of the visible spectrum; identification of the true nature of this radiation; use of undispersed radiation and detectors of low sensitivity; discovery of suitable prisms for extending the limits of the spectrum; development of stronger sources and of detecting devices of sufficient sensitivity to measure accurately dispersed radiation; creation of small rock-salt spectrometers; introduction of echelette gratings for high dispersion; development of automatic research-type high-dispersion spectrometers; and finally, the commercial production of small industrial spectrometers.

2. Applications

Study of the infrared reflection and transmission properties of a few common materials using non-dispersed radiation; use of simple spectrometers for the first study of organic molecules; a thorough study of the physical and mechanical properties of simple molecules such as H_2O , NH_3 , CO_2 , etc.; the application of high-dispersion instruments to the study of pure organic liquids, solids and vapors; qualitative analysis of simple two-component mixtures; quantitative analysis of multicomponent mixtures; and finally, the quantitative analysis and control of research and production samples.

3. Installations

Research in a few isolated laboratories; a spread to a large number of universities, research institutes and foundations; introduction of infrared research into a restricted number of industrial laboratories; and finally, a widespread use of infrared spectrometers both in industrial research laboratories and production plants.

III. THE ELECTROMAGNETIC SPECTRUM

Figure 4 shows diagrammatically the entire electromagnetic spectrum together with the units most frequently used in describing its various re-

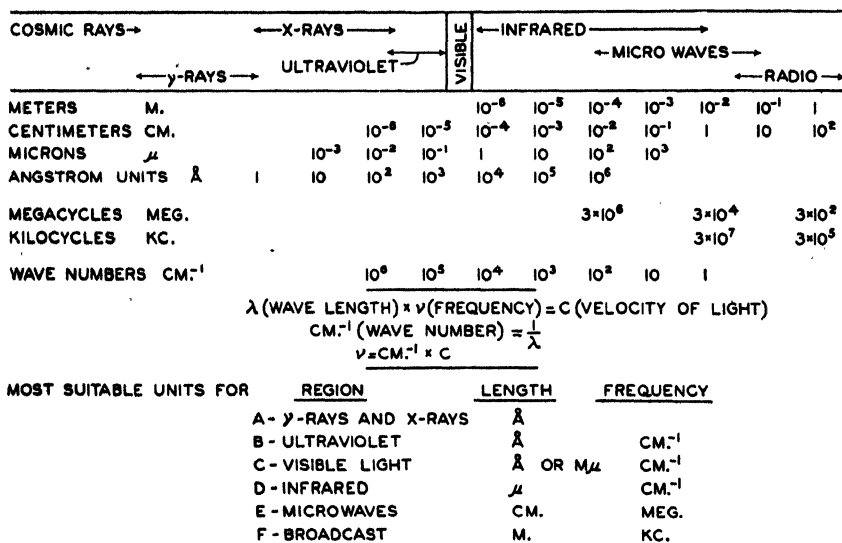


Fig. 4.—The electromagnetic spectrum.

gions and a few fundamental relationships which hold throughout. Although apparently different in their properties and their behaviors toward matter, all portions of the entire spectrum are actually fundamentally equivalent, and may best be described in terms of their inherent wave motion characteristics, namely their wave lengths and/or frequencies. Each portion of this spectrum is useful for analytical purposes, the particular use to which it may best be put being largely determined by its frequency and its penetrating power. Inasmuch as the frequencies of the

radiations of the near infrared* actually correspond to those of the vibrations of the atoms within the molecules, this spectral region is the one of

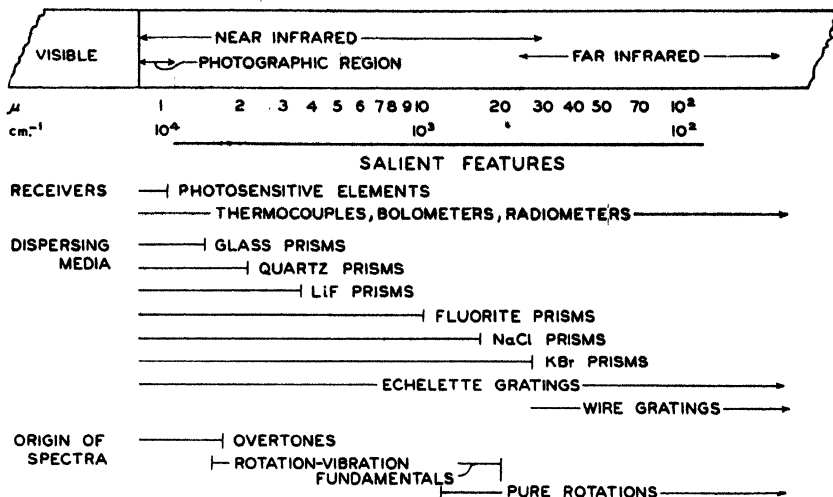


Fig. 5.—The infrared spectrum.

particular significance with regard to the analysis of the structure of organic compounds. Figure 5 presents an extended view of this portion of the spectrum to emphasize a few of its salient features.

IV. ORIGIN OF INFRARED SPECTRA

In any molecule or crystal not at absolute zero, the atoms are constantly oscillating about positions of equilibrium with frequencies, as stated above, corresponding to those of the radiations which compose the near-infrared portion of the spectrum. It can be shown mathematically that such a molecule containing s atoms possesses $3s$ degrees of freedom (5). If from these we subtract 3 for translation of the molecule as a whole, and 3 for rotation (2 if the molecule is linear), it is clear that the molecule has $3s - 6$ ($3s - 5$ if linear) internal degrees of freedom, which can express themselves as normal modes of vibration. According to the degree of geometrical symmetry of the molecule, some of these normal modes may be identical in frequency. Since a normal mode of vibration is defined as one in which the center of gravity of the molecule does not move and in which all of the

* The frequency of 3 μ radiation may be calculated as $\nu = \frac{c}{\lambda} = \frac{3 \times 10^{10}}{3 \times 10^{-4}} = 1 \times 10^{14}$.

atoms move with the same frequency and in phase, each such mode is independent of the others. Thus a given molecule may execute each of these normal modes of vibration simultaneously. The most general form of vibration of such a system can therefore be shown to be one which involves each of these normal modes or fundamentals as well as various overtones and combinations.

Of these vibrations, those which involve a change of dipole moment are infrared active, and are capable of absorbing by resonance all or part of any infrared radiations of corresponding frequency incident upon the molecule. If, therefore, a sample of a single kind of molecule is irradiated in succession by a series of monochromatic bands of infrared, and either the per cent transmission or the per cent absorption plotted as ordinates versus the frequencies of the monochromatic bands as abscissae, the resulting curve enables one to read off at once the values of some of the vibration frequencies of the molecules.

An exact calculation of each of these frequencies, at least those of the complex molecules usually encountered in industry, is a practical impossibility. If such a calculation were possible, however, it would obviously be of very considerable value both in determining organic structures and analyzing mixtures. It is therefore fortunate that the infrared spectrometer furnishes an experimental method for determining these vibration frequencies.

The origin of the intramolecular vibrations referred to above lies in the fact that the atoms of a molecule are constrained to positions of equilibrium by a combination of various forces of attraction and repulsion. The combinations of these forces may be likened to springs holding the respective atoms together. To a first approximation only and strictly for purposes of illustration, these intramolecular vibrations may be assumed to be examples of simple harmonic motion and thus to obey Hooke's Law. To the extent to which this is true, the frequencies* of a diatomic molecule may be calculated by a formula of the type

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \text{ cm.}^{-1}$$

It is interesting to note that, whereas the wave number is not, in the conventional sense of the word, a measure of frequency, it is actually a measure of frequency referred to length. The proportionality constant between the mechanical frequencies and wave numbers is obviously the velocity of light, and the relationship may be expressed as follows:

$$\nu \text{ (vibrations/sec.)} = \nu \text{ (vibrations/cm.)} \times c \text{ (cm./sec.)}$$

where k is the force constant (spring constant) and μ is the reduced mass of the atoms taking part in the vibration. The latter factor is calculated by the relationship $1/\mu = 1/m_1 + 1/m_2$, where m_1 and m_2 are the masses of the vibrating atoms. Upon substituting the proper universal constants into the above vibration equation, the frequencies expressed as wave numbers (cm.^{-1}) may be calculated from the simplified relationship

$$\nu = 1307 \sqrt{k'/\mu} \text{ cm.}^{-1}$$

in which k' is used as a pure number divided by 10^5 , and μ is expressed in dimensionless atomic mass units. The literature (6) shows that the value of k for practically all single bonds lies between 4 and 6×10^5 dynes per cm. , whereas that for double bonds falls between 8 and 12×10^5 , and for triple bonds, between 12 and 18×10^5 dynes per cm.

As an illustration of a diatomic molecule, if k is taken as 5×10^5 dynes per cm. and μ as 1 , we calculate

$$\nu_{\text{HCl}} = 1307\sqrt{5/1} = 2920 \text{ cm.}^{-1}$$

The experimental absorption curve for this molecule shows a strong vibration fundamental at 2890 cm.^{-1}

In all molecules possessing three or more atoms, various interactions which depend upon the simultaneous motions of all of the atoms and the forces which each atom of the molecule exerts upon every other atom, the simple equation used above is even less exact. It is, however, interesting to note below the extent to which approximate agreement is found between the calculated and observed vibration frequencies for certain atom pairs within more complex molecules. For the C—H vibration in methane, the value of k has been found to be almost exactly equal to 5×10^5 dynes per cm. Since the carbon atom is heavy in comparison with hydrogen, the value of μ remains very close to unity. Thus:

$$\nu_{\text{CH}} = 1307\sqrt{5/1} = 2920 \text{ cm.}^{-1}$$

For the CO in methyl alcohol, k is also close to 5×10^5 dynes per cm. The value of μ , however, rises to 6.85 , so

$$\nu_{\text{CO}} = 1307\sqrt{5/6.85} = 1110 \text{ cm.}^{-1}$$

Analogously for C=O in acetone,

$$\nu_{\text{C=O}} = 1307\sqrt{12/6.85} = 1730 \text{ cm.}^{-1},$$

and for C≡N in HCN,

$$\nu_{\text{C}\equiv\text{N}} = 1307\sqrt{15/6.5} = 2000 \text{ cm.}^{-1}$$

An examination of the absorption spectra of these four compounds reveals strong bands at 2915, 1034, 1744 and 2089 cm^{-1} , respectively. It can also be demonstrated that these and other characteristic group frequencies may be recognized in the spectrum of almost any organic molecule containing these atom pairs. We see, therefore, that while these simple calculations are not exact, they do in fact allow one to predict roughly in which region of the spectrum the absorption of a given group might be expected to fall. The slight variations observed in the exact frequencies of maximum absorption for molecules which are closely related chemically—and so exhibit only slight differences in k and μ —often make it possible to determine empirically not only that a certain atom group is present, but also to predict the relationship of this group to the remainder of the molecule.

TABLE I
TYPICAL INTERATOMIC CHARACTERISTICS^a

Atom pair	Reduced mass	k	Interatomic distance Å	Absorption frequency, cm^{-1}	Compound
C—C	6	4.50	1.54	993	C_2H_6
C—O	6.85	5.77	1.43	1034	CH_3OH
C—N	6.46	...	1.47	1045	CH_3NH_2
C=C	6	9.77	1.33	1623	C_2H_4
C=O	6.85	12.06	1.21	1744	H_2CO
C=N	6.46	...	1.26	1653	CH_3CHNOH
C≡C	6	17.2	1.20	1975	C_2H_2
C≡O	6.85	...	1.10	2169	CO
C≡N	6.46	16.6	1.15	2089	HCN
C—H	0.92	5.07	1.07	2915	CH_4
O—H	0.94	...	0.96	3683	CH_3OH
				3370	
N—H	0.93	...	1.00	3315	CH_3NH_2
S—H	0.97	...	1.31	2597	CH_3SH

^a Values taken from published literature.

Table I shows the influence of k and μ upon the interatomic distances and the vibration frequencies of certain atom pairs. This table is intended merely to illustrate the origin of infrared vibration absorptions, and by no means as a complete tabulation of the characteristic frequencies so far identified.

As may be expected from analogy with other vibrating mechanical systems, weaker absorption bands may also be observed for various of the many overtones and combinations of the fundamental frequencies. While these in some cases lead to a certain degree of confusion in the proper identi-

fication of the fundamentals, they more often aid greatly by imparting unique characteristics to the complete infrared spectrum of any given organic molecule.

Throughout the electromagnetic spectrum, the fundamental relationship which determines the passage of radiation through a transparent medium or sample of thickness x , is known as Beer's law. This may be expressed as

$$I = I_0 e^{-kcx}$$

where the terms are as follows: I = intensity of radiation transmitted; I_0 = intensity of radiation incident on sample; e = base of the natural logarithms; k = specific extinction coefficient, a function of the frequency ν and specific for each molecule; c = concentration of sample; and x = thickness of sample. Since I/I_0 = per cent transmission = T , we can rewrite Beer's law as

$$\log 1/T = kcx.$$

This expression forms the basis for all "colorimetric" analyses, whether ultraviolet, visible or infrared. If T can be measured through the use of a suitable spectrometer and x determined, the product of k (qualitative chemistry) and c (quantitative chemistry) is obtained directly. Thus, if the spectrum of a pure sample ($c = 100$) is measured, we obtain once and for all the value of k for each frequency ν . Analogously, if k for a given compound is known, the per cent transmission at a frequency where k is large leads directly to the corresponding value of c .

Except where chemical reactions take place between components, the spectrum of a mixture is the summation of the spectra of the individual components. For most mixtures, therefore, the transmission at ν may be expressed as

$$\log 1/T_\nu = (k_\nu c_1 + k_\nu c_2 + \dots k_\nu c_n)x.$$

Actually, as a result of the experimental conditions under which infrared spectra must be obtained, Beer's law may be expected to hold precisely only in exceptional cases. Since deviations from this law, however, are usually small and can be determined experimentally, suitable allowances may, if necessary, be introduced into the calculations.

Roughly speaking, an infrared spectrum of per cent transmission may be said to yield qualitative information through its abscissae (frequencies of maximum k values) and quantitative information through its ordinates (exact values of T at selected frequencies where absorption is caused primarily by the specific compound for which the analysis is being performed).

V. EXPERIMENTAL APPARATUS AND TECHNIQUES

From the above it is clear that the infrared spectrometer must measure the per cent transmission of a sample at each of a wide variety of frequencies. The value of such an instrument is determined by the accuracy of measurement and the narrowness of the bands of frequencies at which measurements can be made. So many types and designs of instrument are in use today that it will be impractical to attempt to describe them all. This discussion will, therefore, be limited to a brief description of one each of two types, namely, one large research model and one small routine instrument.

Figure 6 shows schematically the optical path of the original research spectrometer which has been in use in this laboratory for the past seven years (7).

The spectrometer proper should be self-explanatory. Focusing mirrors, M_2 and M_3 , have focal lengths of 60 cm., while the collimating mirror, M_4 , has a focal length of 40 cm. The double galvanometer relay shown at the lower left has been described several times. Light from S is focused by lens L_1 on the mirror of galvanometer G_1 which is connected to the thermocouple. L_2 focuses this light onto photocell Pc , the output of which drives galvanometer G_2 . The motion of the beam of light reflected from the mirror of this galvanometer is recorded by the "fountain pen" recorder.

As designed and operated, the instrument is satisfactory for use from the visible spectrum out to about 750 cm.^{-1} or $13\text{ }\mu$. Since a rock-salt prism is employed, the dispersion around 3000 cm.^{-1} ($3.3\text{ }\mu$) is relatively low, the spectral slit width being approximately 20 cm.^{-1} . For a prism-type spectrometer, this instrument may be said to be of the high-dispersion type. The use of a potassium bromide prism would extend its range to about 500 cm.^{-1} , with an attendant decrease of dispersion in the 1600 cm.^{-1} region, whereas the use of a lithium fluoride prism of equal size would increase the dispersion in the 3000 cm.^{-1} region by a factor of about 5, but would limit the range at about 2800 cm.^{-1} .

Typical of all infrared spectrometers are: the source, an electrically heated incandescent solid (in this case a Globar having a power consumption of about 400 watts at 115 volts); front surface aluminized mirrors for collecting, collimating and focusing the radiation; and a sensitive thermoelectric radiation detector. In this particular instrument, the collimating mirror, M_4 , is a sphere kept on the optic axis by using the slotted plane mirror, M_5 . Two 10-cm. rock-salt prisms* are used in tandem in a Littrow

* The use of two prisms was necessitated by the limited size of salt crystals available when this instrument was constructed in 1936.

mount and frequencies are varied by rotation of the plane Littrow mirror, M_6 . The detector is a single-junction vacuum thermocouple whose electrical output is amplified by a two-galvanometer-photocell relay and recorded by means of a dual-cathode phototube thyratron controlled fountain pen recorder (8). The entire instrument is housed in a thermally lagged aluminum case which can be partially dried by circulation of air previously passed over numerous trays of phosphorus pentoxide. Radiation from the source enters and leaves the spectrometer case, where necessary, through rock-salt windows.

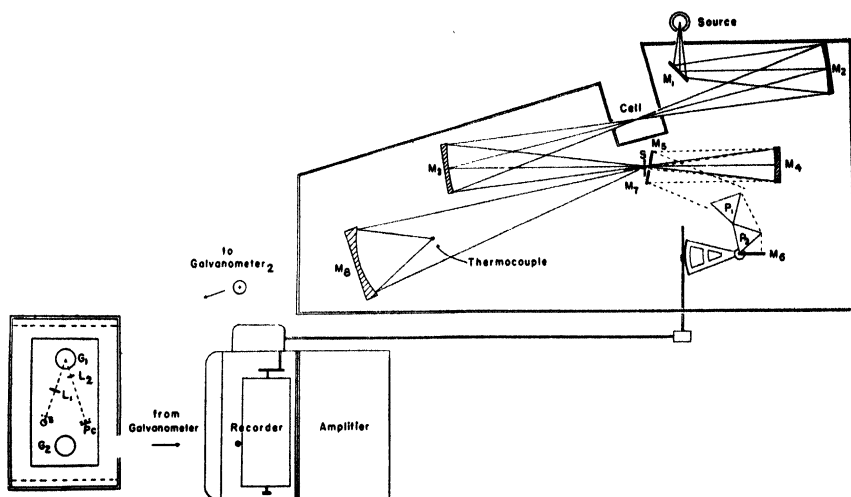


Fig. 6.—Schematic drawing of a research-type infrared spectrometer.

The average energy in the dispersed beam of radiation produces at the junctions of the thermocouple about 1 microvolt. Accordingly, to measure a given transmission value to one-half of one per cent, the electrical system of the instrument must be capable of detecting with accuracy changes as low as 5×10^{-9} volts. Since the thermoelectric coefficient of the materials used in the thermocouple is about 100 microvolts per degree Centigrade, it is clear that temperature changes in the thermocouple junctions must be measured which are of the order of 5×10^{-8} degree Centigrade. Small changes in ambient temperature are minimized by using a compensated or two-junction thermocouple connected in series opposition, only one of the hot junctions of which receives the radiation to be measured. Because the values measured are minute, extreme care must be exercised to mount the

galvanometers so that they are free from vibrational disturbances, to shield the spectrometer electrically and thermally and to prevent the thermocouple from "seeing" any stray radiation from the walls of the spectrometer or the jaws of the slits.

The average transmission curves taken on this spectrometer are of sufficient accuracy for most research purposes. The transmission values themselves may be measured to about $\pm 1\%$ and the frequency values may be determined to $\pm 5 \text{ cm.}^{-1}$ from suitable calibration data. The operation of this instrument is relatively simple, and a galvanometer deflection record may be obtained over the useful spectral interval in about 40 minutes. From this record, the final transmission curve if needed may be calculated in per cent and hand-plotted in an additional three hours.

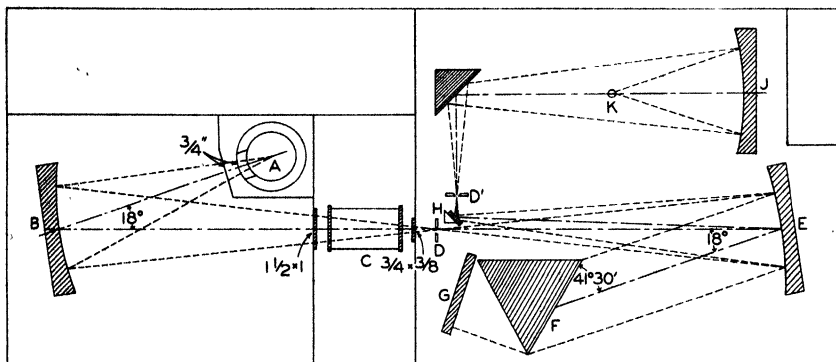


Fig. 7.—Schematic drawing of a small prism infrared spectrometer. The optical path of the radiation from source A to the focusing mirror B through absorption cell C and through the Littrow spectrometer to thermocouple K may be traced readily.

For a detailed description of this and other research spectrometers having unique advantages, the reader is referred to the literature (7, 9, 10).

As stated above, important industrial analyses can be performed with a small abridged infrared spectrometer. During the past few years several such types have been designed and described (11, 12).

Figure 7 shows a schematic diagram of one such spectrometer (11). This instrument, a typical 60° rock-salt prism Littrow spectrometer, has an aperture of $f 3.5$, a Globar source, a readily accessible position for the absorption cell (up to 10 cm. in length), a compensated permanently evacuated thermocouple, a micrometer frequency (wave length) adjustment and a set of hardened steel stops for setting the instrument quickly to selected frequencies. Its over-all length is only about 30 inches; and, when used

with a sensitive galvanometer (Leeds and Northrup, HS type) and scale, it offers many possibilities as a tool for analysis and control.

Discussions of the usefulness and applicability of each of the spectrometer types described above are given in several recent papers (7, 11-16) which also present detailed descriptions of techniques best suited for infrared analyses of a wide variety. Suffice it to state here that by following the procedures outlined for the particular type of problem at hand, satisfactory results can be obtained whether the sample is a solid, a liquid or a gas. As seen from Beer's law, the measurement which is usually desired for analytical purposes is the per cent transmission at some one or more specific frequencies.

This value may be obtained readily by setting the spectrometer at the correct frequency, and then measuring the energy transmitted (galvanometer deflection) through the absorption cell both when it contains the unknown sample and when it is empty (a duplicate cell is frequently used for this measurement). The ratio of these two deflections or energies gives the desired value, after suitable corrections have been made for the energy scattered by the spectrometer, for the absorption of the cell windows, etc. Assuming that these measurements can all be made, an analysis may be performed either by Beer's law calculations or by using a previously determined work curve of the per cent transmission of the material in question as a function of its concentration in the other components of the sample. So many modifications of these techniques are in use that the reader is again referred to the detailed literature.

Absorption cells also vary widely, and their lengths range from many centimeters, for gases, to only a few microns, for certain liquids having strong absorptions. The determination of the exact thickness of the cell to be used often presents considerable difficulty. A typical liquid cell may be formed by two flat rock-salt plates clamped rigidly together and separated by a U-shaped spacer of metal foil, the cell thickness being assumed to equal that of the metal foil.

VI. TYPICAL CHEMICAL APPLICATIONS

Equipped with a satisfactory spectrometer and a knowledge of the various techniques, an infrared spectroscopist may approach with confidence organic analyses of many types, some of which will be described below. In general, these analyses may be divided into two basic categories, qualitative and quantitative. The speed with which these analyses can be performed, the smallness of the sample required, and the very fact that the origin of the absorptions used lies in the mechanics of the molecule—and

so is a function of the geometry and spatial structure of the molecule being examined—make the infrared method one of the more important analytical procedures.

1. Qualitative Applications

A. "FINGERPRINTING" OF MOLECULES

The infrared spectrum of a pure compound is unique and cannot be duplicated by any other compound. Accordingly, such spectra provide qualitative identification of an unknown pure compound in much the same

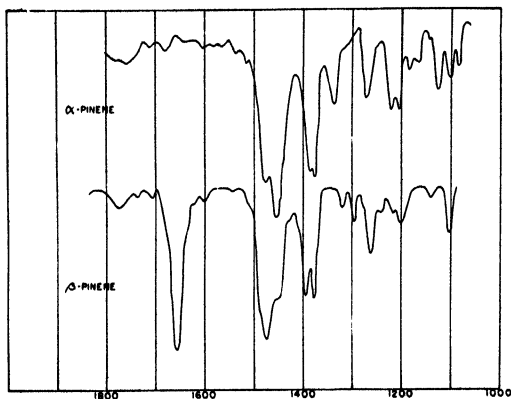


Fig. 8.—Transmission curves for α - and β -pinene.

manner as a fingerprint. If the characteristic spectra of a large number of compounds are available, the identity of an unknown may often be established within a few minutes. The procedure is to find the counterpart of the unknown spectrum by comparison with the known spectra. All spectra used for comparison should have been obtained with the same spectrometer, or at least one of similar performance. This requirement arises from the fact that each instrument is characterized by a different scattered radiation factor, resolving power and degree of reproducibility.

Figure 8 shows two such reference spectra. From them, slight structural differences are seen to cause pronounced spectral differences.

Even where no satisfactory match can be found between the spectrum of the unknown and that of any available known, the positive knowledge that the unknown is not identical with any of the knowns is information of analytical importance.

This simple method is of great value in research and in production where the analytical problem is to determine the equality of successive produc-

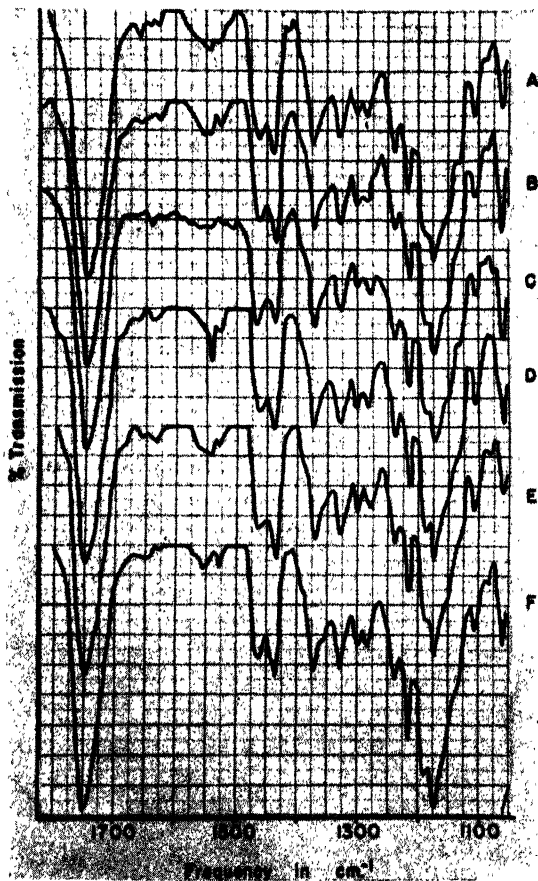


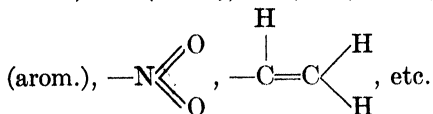
Fig. 9.—The use of infrared for qualitative identification.

tion batches of a given material or several samples purported to be identical. Figure 9 illustrates this use of infrared spectra.

The samples were prepared by different chemical methods and were presumed to be different molecules. The similarity of the spectra proves that they are, with the exception of a few minor impurities, all of the same structure.

B. ANALYSIS FOR SPECIFIC CHEMICAL BONDS, GROUPS OR LINKAGES

Infrared spectra of organic liquids are characterized by absorption bands which repeatedly occur at specific frequencies. These can be correlated empirically with the presence of certain bonds or atomic groups within the molecule. Thus it is generally possible by careful examination of the infrared spectrum of an unknown sample to recognize at least some of the chemical linkages present. The analytical importance of this type of information lies in the fact that usually the supposed structure of a molecule can be confirmed or denied by the presence or absence of some one functional group. Fortunately, the atomic groups causing the most readily identified infrared absorptions are the most important from a structural chemical point of view. Among these are the following: OH, NH₂, =NH, CH (arom.), CH₃, SH, C≡N, C≡C, C=O, C=C (aliph.), C=C



Partial explanation of this is given above and in the data of Table I (page 134). The remainder of the molecule usually produces only a slight effect upon the vibration frequencies of certain groups or pairs of atoms, thus leaving them truly characteristic of the group. It is fortunate for the analyst, however, that not all of the 3s — 6 fundamentals of a molecule are thus characteristic of individual atomic groups, for the fingerprint method described above depends primarily upon frequencies extremely sensitive to subtle changes in the structure of the molecule as a whole.

C. RECOGNITION OF GROSS STRUCTURAL FEATURES

A third qualitative method is an extension of method B above. Frequently the geometrical arrangement of the atoms within a molecule may be determined by the presence of certain groups of absorption bands. Thus a decision can usually be reached as to whether a molecule is *cis* or *trans*, ortho-, meta- or para-, enolic or ketonic, monomeric or polymeric, etc. For example, Figure 10 illustrates the spectral differences of three isomers.

D. ANALYSIS OF MIXTURES

The organic analyses most frequently required are qualitative answers to such questions as "Does it contain any aromatic compound?", "Does it have any hydroxyl or amino groups?", "Does it contain any polymeric material?", etc. Furthermore, the average sample received by the spectro-

copist is either impure or definitely a mixture of several components. For qualitative analysis of such samples, infrared offers many outstanding advantages.

If no chemical reaction has taken place, the infrared spectrum of a mixture is equivalent to a simple superposition of the spectra of the individual

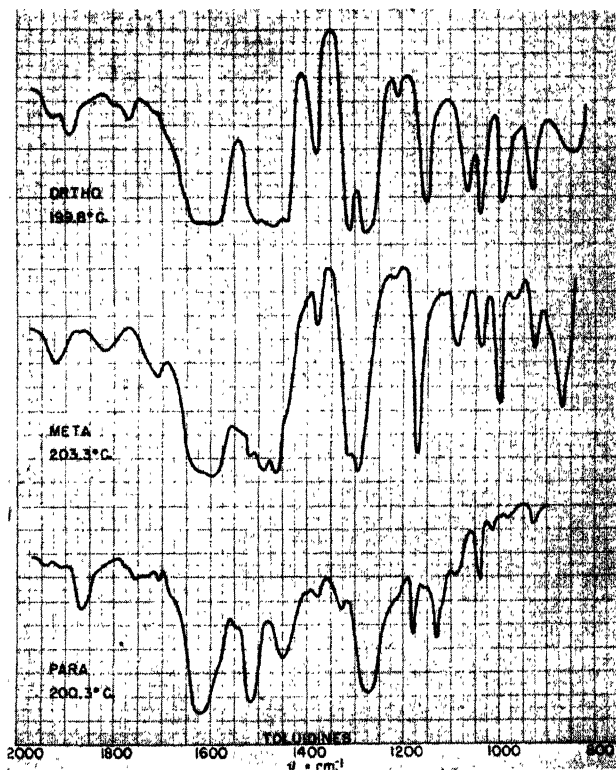


Fig. 10.—Transmission curves for *o*-, *m*-, and *p*-toluidines illustrating the spectral differences produced by isomerization.

components. Therefore, if the spectrum of a given molecule has been recorded as part of a library of spectra, inspection will show whether it forms a part of the spectrum of the mixture. If it does, a rough estimate of its concentration in the mixture is readily obtained.

2. Quantitative Applications

A. ANALYSIS OF MIXTURES

If all of the components of a mixture have been identified qualitatively, it is possible to analyze it quantitatively by means of its infrared spectrum. Several techniques for quantitative analyses have recently been described in the literature (17, 7, 14). The first step in all such analyses is a study of the spectrum of each component individually in order to select the proper frequencies for the analysis of the mixture. As far as possible, each frequency chosen should be one at which only a single component shows strong absorption. By setting the spectrometer successively at each of the selected analytical frequencies and comparing the absorption of the unknown with that of a set of known prepared standards, the amounts of each component can be determined.

Modifications of this procedure are required in many specific cases (17, 7, 14). Frequently, for example, it is impossible to find analytical frequencies at which only one component absorbs. In such cases, methods of successive approximations are employed. Quantitative applications of Beer's law, and many examples of specific analyses—ranging from simple two-component systems to the more important cases of multicomponent complex mixtures—have been described in the literature.

The degree of accuracy obtained is a function of the spectrometer used, the particular technique employed and the nature and complexity of the samples themselves.

B. MEASUREMENTS OF REACTION RATES

Since, in chemical reactions, certain chemical bonds are broken and others are formed, application of the principles of quantitative analysis referred to above permits surprisingly accurate measurement of the rate of the reaction. The spectrometer may be set at a characteristic frequency which either appears or disappears during the reaction, and the per cent transmission measured as a function of temperature, time, pressure, etc. Obviously, for this type of determination, the reaction must be slow enough to allow samples to be withdrawn from the reaction chamber and introduced into the spectrometer before any further changes in their structure or composition have taken place. By referring the data thus secured to a work curve which has previously been determined for the particular reaction in question, the desired information is obtained. Figure 11 shows such a determination in the case of the polymerization of styrene.

(A) is the change of the 1628 cm^{-1} absorption band with time of polymerization. (B) is the per cent transmission at 1628 cm^{-1} versus reaction time. (C) is the per cent transmission at 1628 cm^{-1} versus per cent monomer of samples prepared

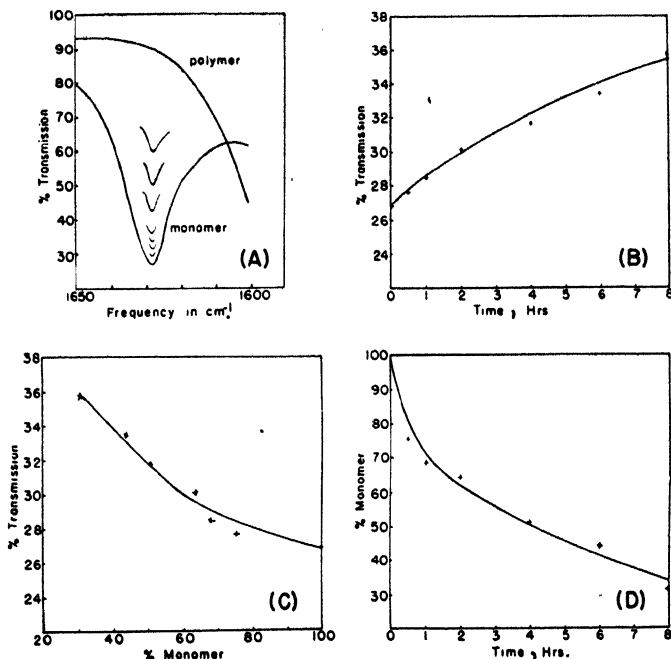


Fig. 11.—Infrared determination of rate of polymerization of styrene.

for purposes of calibration. (D) is the per cent of monomer versus reaction time calculated from transmission values at 1628 cm^{-1} .

C. PROCESS CONTROL AND ANALYSIS

Many plant processes can be characterized by the presence or absence of some one functional group in the product. This group may be included in the desired end product or in some particular unwanted impurity. Continuous measurement of the per cent transmission at a single frequency previously found unique for the group in question may be used directly as an indication of the progress or success of the reaction. Gaseous samples may be by-passed from the production line through the absorption cell. By using suitable amplifiers, the output of the infrared detector can in certain

cases not only indicate the result of an analysis but also actuate automatic control mechanisms.

VII. FUTURE POSSIBILITIES

This account of infrared spectroscopy suggests the role which it is destined to play in future chemical research and analysis. The technique is unique in obtaining information concerning molecular structure, and both qualitative and quantitative analyses from small samples of solid, liquid or gaseous substances. The simplicity and speed of the method, together with its adaptability to problems of industrial control, also add materially to its value.

The development of this branch of physics, having passed through several important and definite phases, has now arrived at its most practical and fruitful stage. It is ready now to be used by research workers in an increasing number of branches of science—both academic and industrial. New modes of application and improved techniques will be worked out whereby still greater sensitivity, speed, accuracy and reliability will be achieved, and structure problems of even greater complexity will yield to solution.

In the future, the details of design of the spectrometer itself will play an increasingly important part. It is fortunate, therefore, that the assistance of the instrument maker has been enlisted. No longer will each infrared spectrometer be one of a kind, the creation of an individual spectroscopist. A variety of instruments will be commercially available for use—but each type will have been carefully designed and accurately constructed. The infrared spectrometer will be a scientific tool of ever-increasing value and importance.

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